LA-UR-14-27226
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Title:	Investigation of light-matter interactions: Photoluminescence properties of individual quantum emitters
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Intended for:	Progress meeting for a possible collaboration
Issued:	2014-10-22 (Rev.1) (Draft)

Investigation of Light-Matter Interactions: Photoluminescence Properties of Individual Quantum Emitters

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EST.1943
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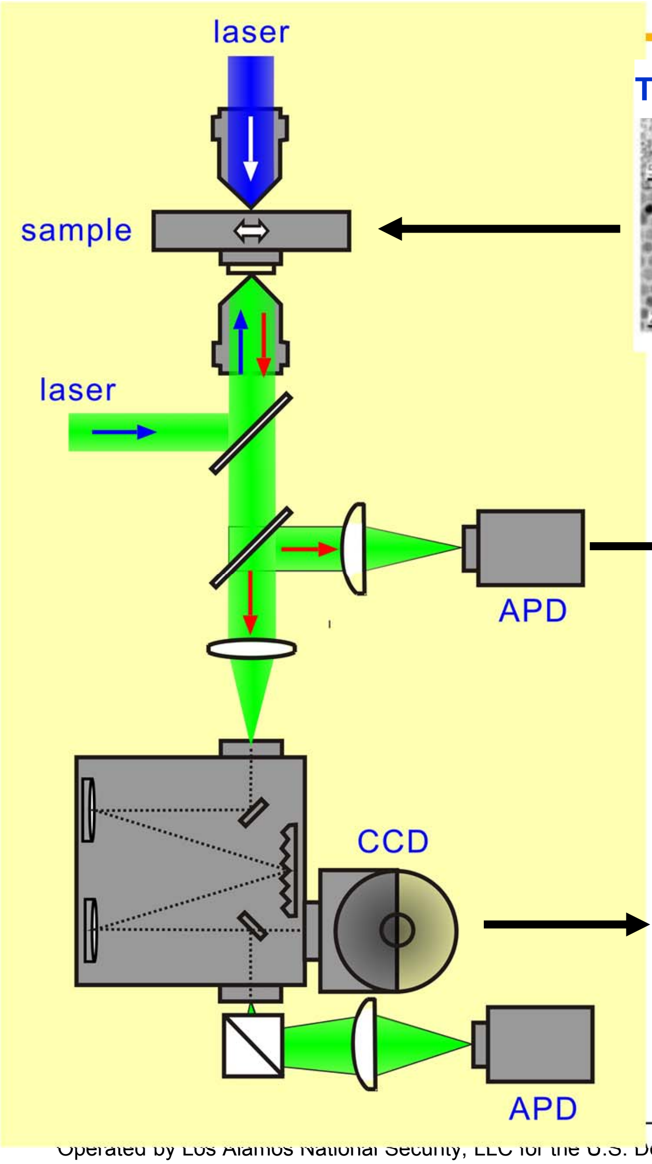
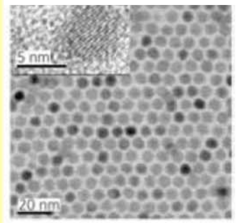
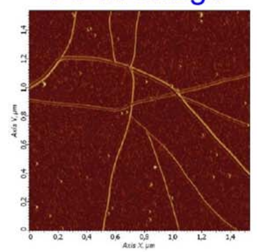
Research Techniques



TEM/SEM image

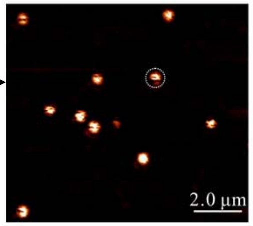


AFM image

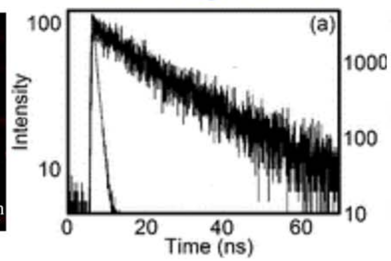


- PL/Raman/Rayleigh scattering measurements
- Laser: CW/pulsed, ultrafast
- cryogenic measurements
- E-beam/photo-lithography

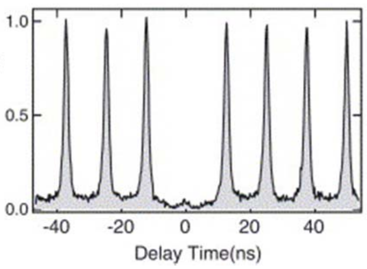
PL image



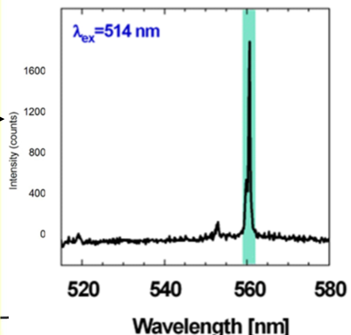
PL decay curve



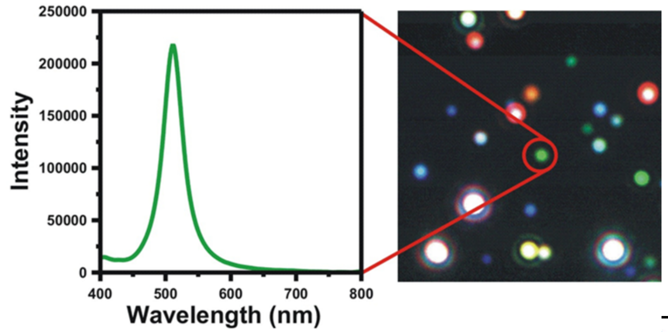
Photon statistics



Raman spectrum

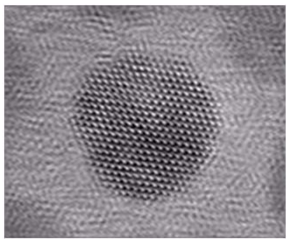
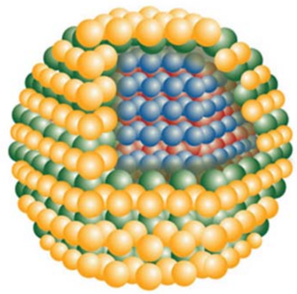


Scattering spectrum and image

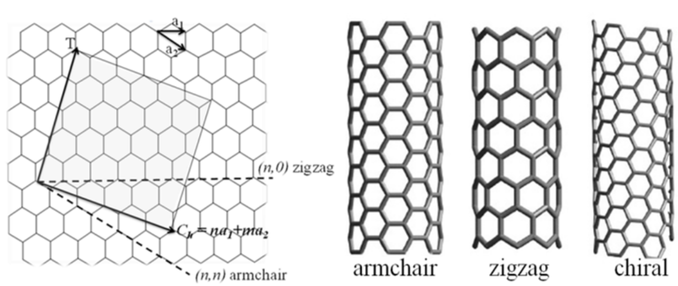


Mainly Studied Topics

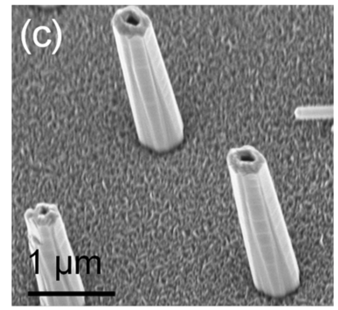
II-VI semiconductor quantum dots (QDs)

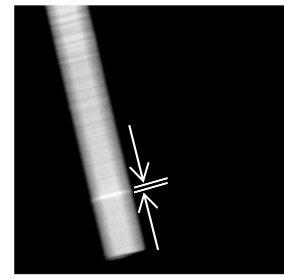
Single-walled carbon nanotubes (SWCNTs)



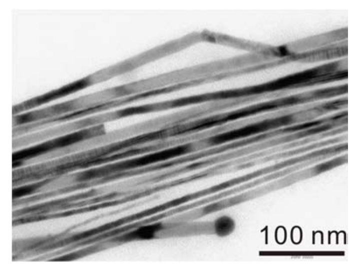
Semiconductor nanotubes/nanowires



ZnO nanotubes

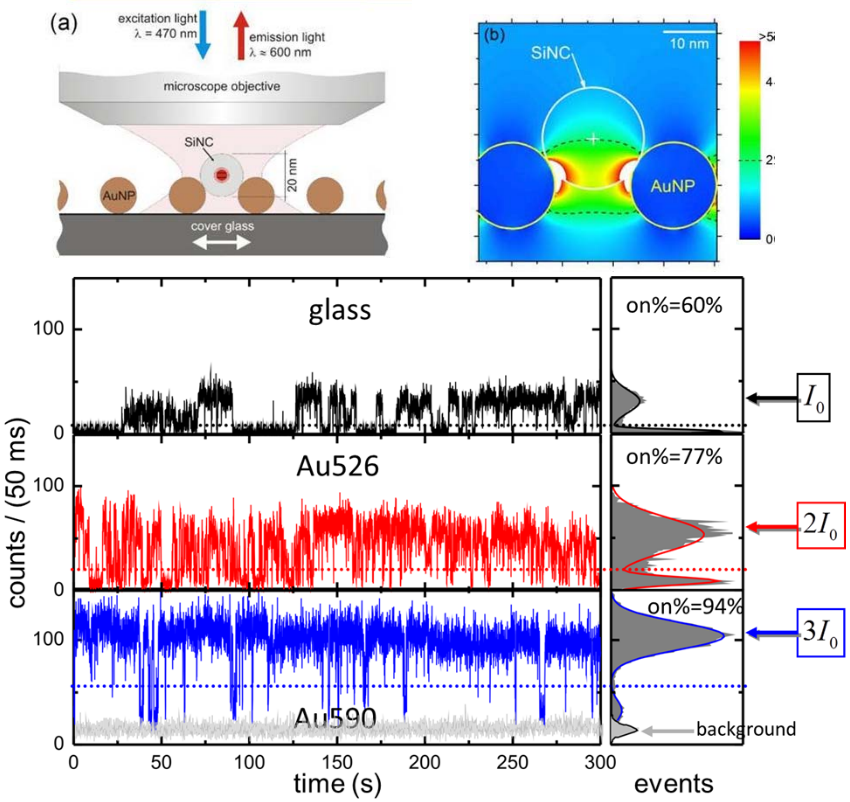


GaAs QDs in GaAsP pillars

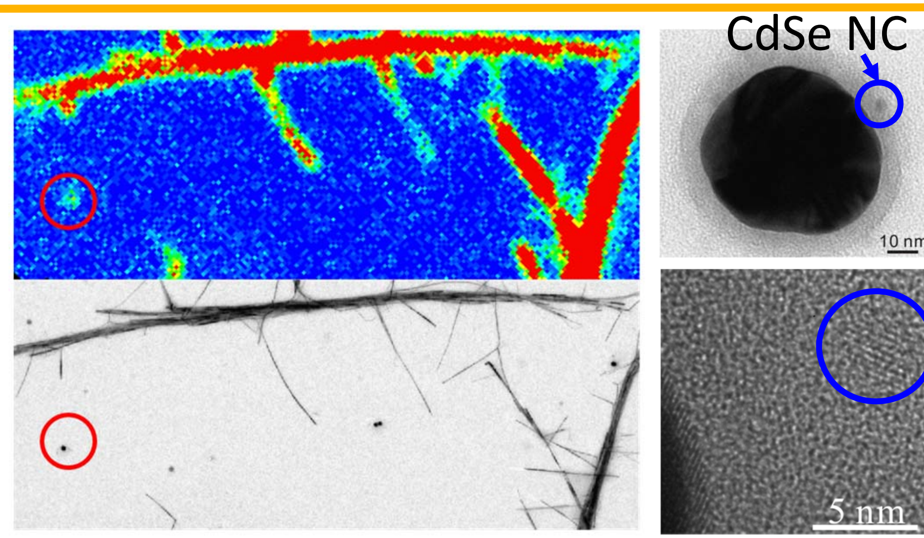


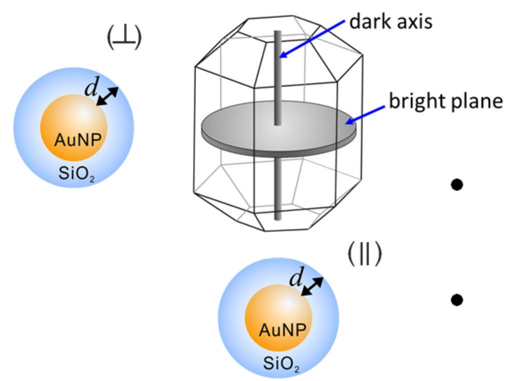
CdSe nanowires

QDs Coupled to Surface Plasmons



- enhanced PL intensity
- suppressed blinking
- gray states

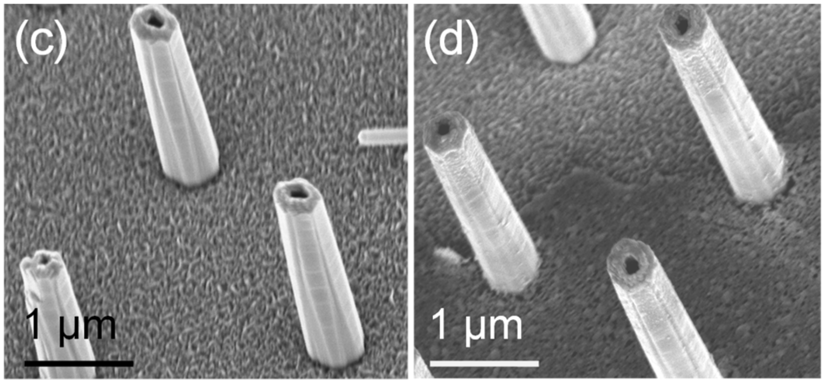




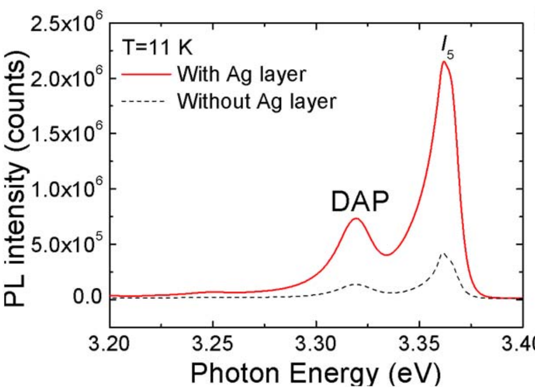
- Lifetime decreases with d.
- Lifetime is dependent on dipole orientation.

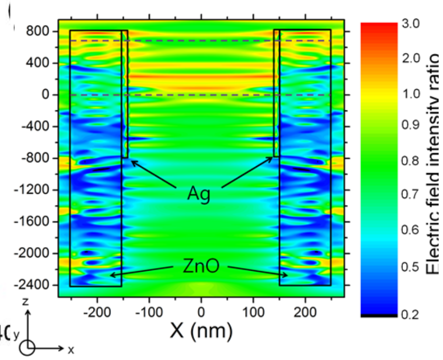
Ma et al. Nano Lett. 2010, 10, 4166
Ma et al. J. Phys. Chem. Lett. 2011, 2, 2466
Ma et al. J. Phys. Chem. C 2013, 117, 16698

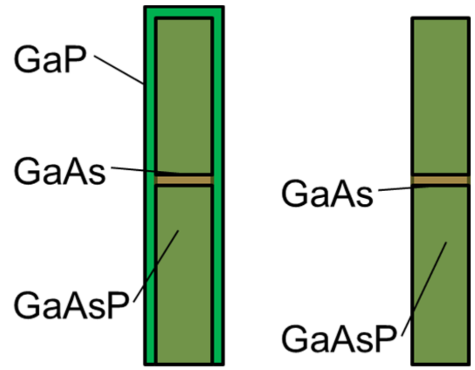
Semiconductor Nanotubes/Nanowires

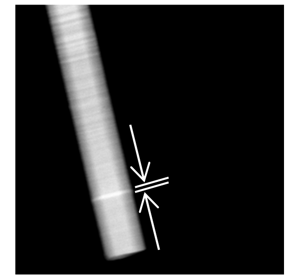


ZnO NT   ZnO NT + Pt (inner)



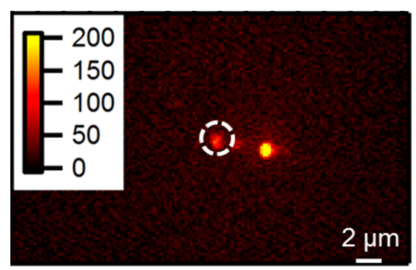




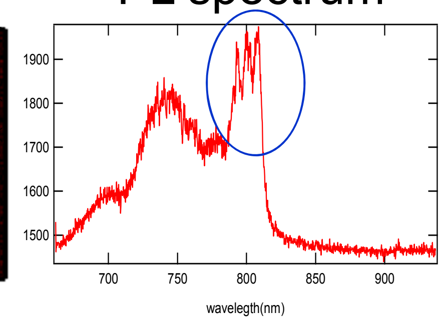


Courtesy of Liang

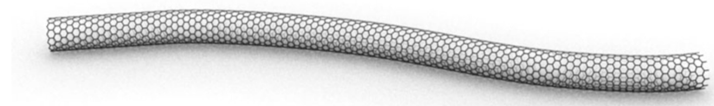
PL image



PL spectrum



Z. Li, X. Ma et al. Eur. J. Inorg. Chem. 2010, 27, 4325
Z. Wang, X. Ma et al. Small 2011, 7, 2464
J. Yoo, X. Ma et al. Nano Lett. 2013, 13, 2134



PL of Single-Walled Carbon Nanotubes

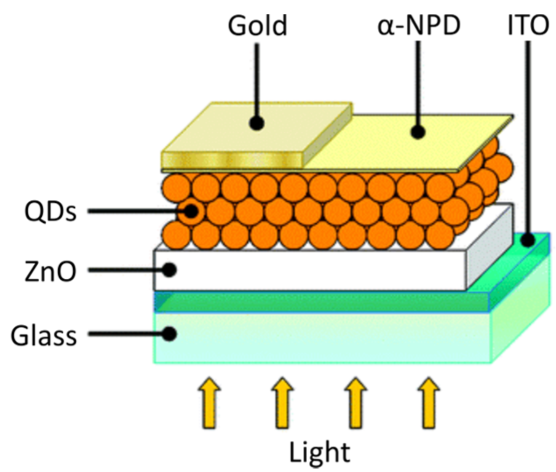
- Photon Statistics of Individual Carbon Nanotubes at Room Temperature
- Oxygen Doping Modifies Excitonic Fine Structures of Carbon Nanotubes
- Influence of Exciton Dimensionality on Spectral Diffusion of Single-Walled Carbon Nanotubes

Photon Statistics of Individual Carbon Nanotubes at Room Temperature

Ma et al. Phys. Rev. Lett. in submission

Why Photon Statistics?

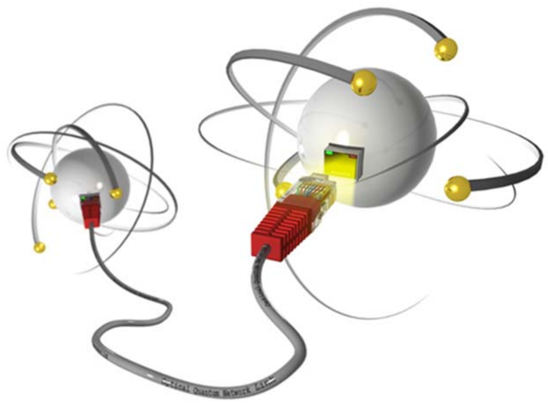
photovoltaics and solar cells



ACS Nano, 3, 3638–3648 (2009), Aydil et al.

- multiexciton generation rate

quantum information

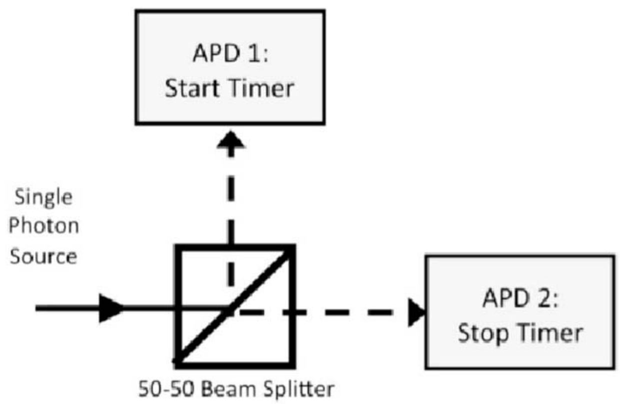


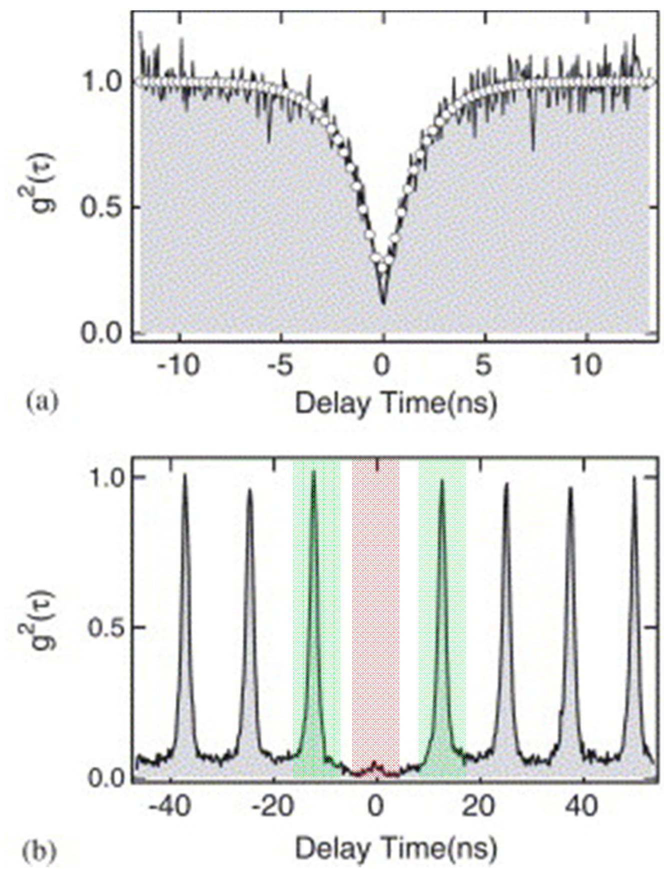
A. Neuzner, MPQ
Nature, 484, 195 (2012), Ritter et al.

- single photon source

Second-order Correlation Function $g^{(2)}$:

Hanbury-Brown-Twiss Setup





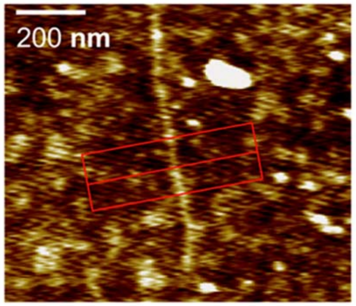
CW laser

Pulsed laser

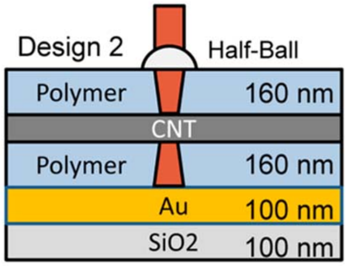
$(R = I_{center}/I_{side})$

- $g^{(2)}$: a measure of photon statistics.

Photon Statistics of CNTs: State of the Art



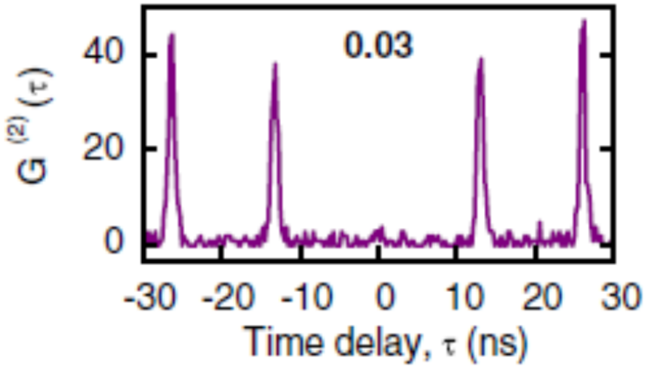
4.2 K



9 K

PRL 100, 217401 (2008), Hoegele et al.

Nano Lett. 12, 1934 (2012), Stefan et al.



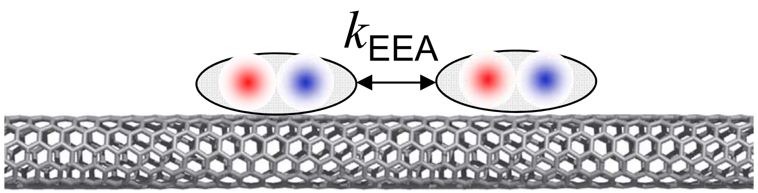
$R < 0.5$

photon antibunching

- Photon antibunching: photons are separated from each other.

Photon Statistics of CNTs: Mechanism

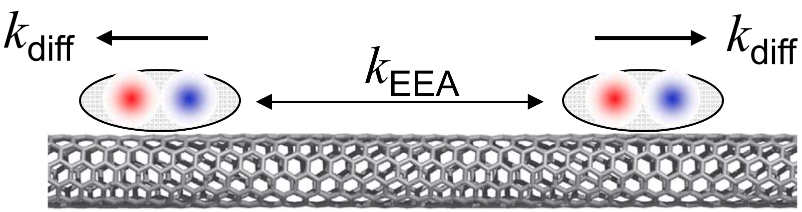
Low T



localized exciton:

- exciton – exciton annihilation (EEA)

Room T

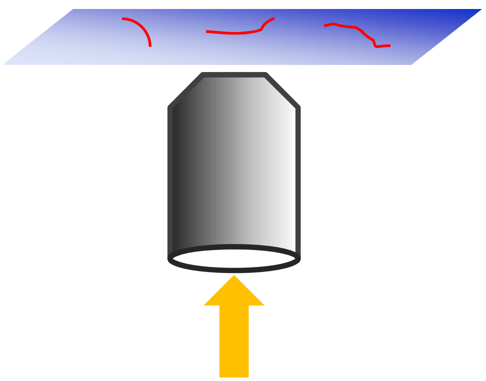


diffusing exciton:

- exciton – exciton annihilation (EEA)
- exciton diffusion

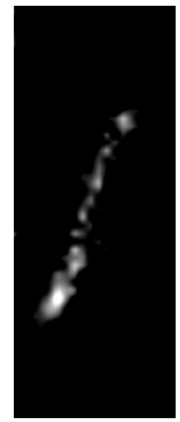
How exciton diffusion and EEA affect photon statistics in 1D system?

Individual SWNT Imaging



Wide field images

Stable PL

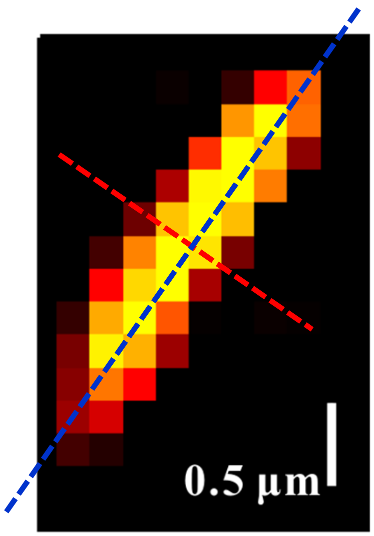


PL blinking/fluctuation

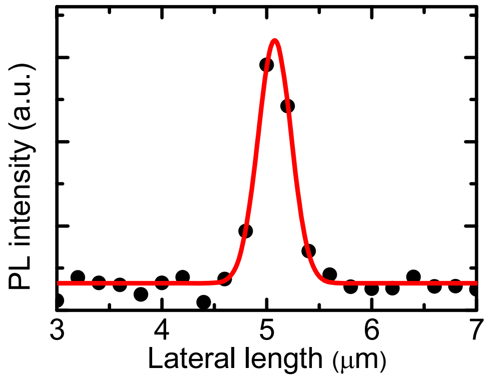
- Homogeneous illumination of the whole SWNTs with expanded laser beam
- Beam size: ~60 x 60 um
- SWNT length: <15 um

Individual SWNT Imaging

Wide field image



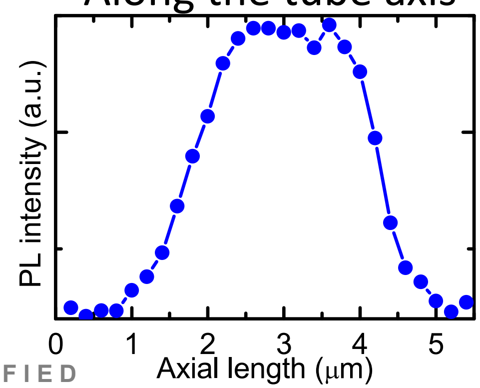
Perpendicular to the tube axis



width (@$1/e^2$)
= 635 nm

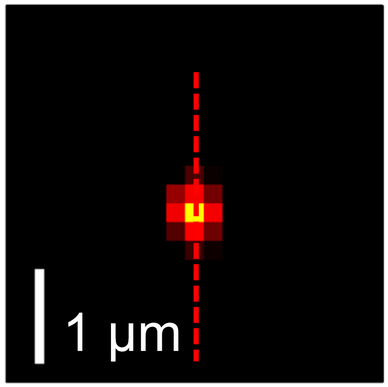
- Fitted with a Gaussian function
- Diffraction limited

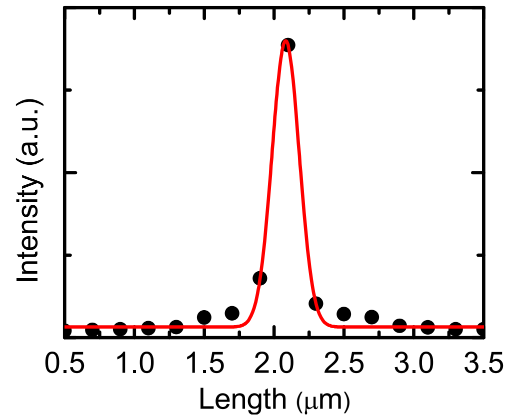
Along the tube axis



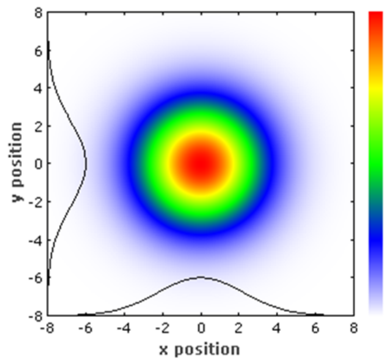
L ~ 4.2 um

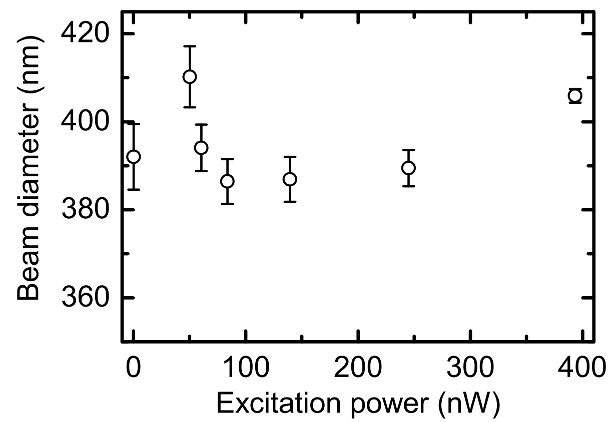
Gaussian Laser Spot





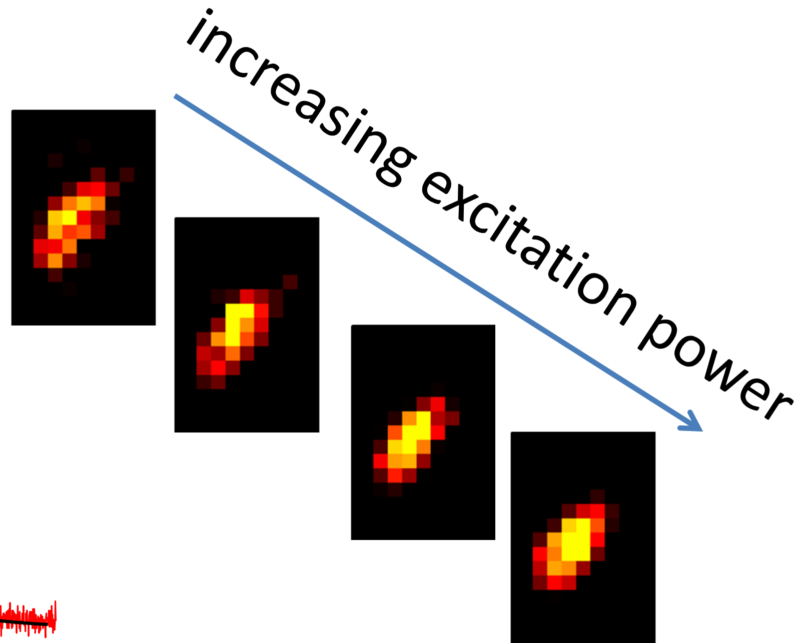
- Fitted with a Gaussian function
- Diffraction limited

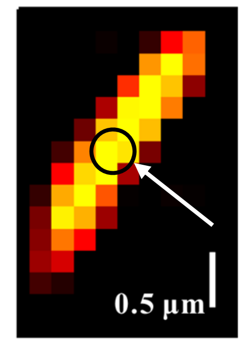


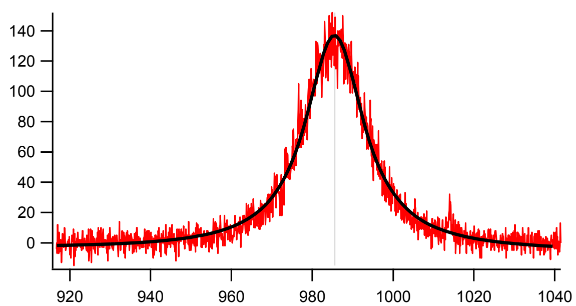


- Beam size independent of power.

Excitation Power Dependent PL images



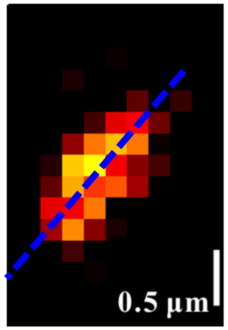


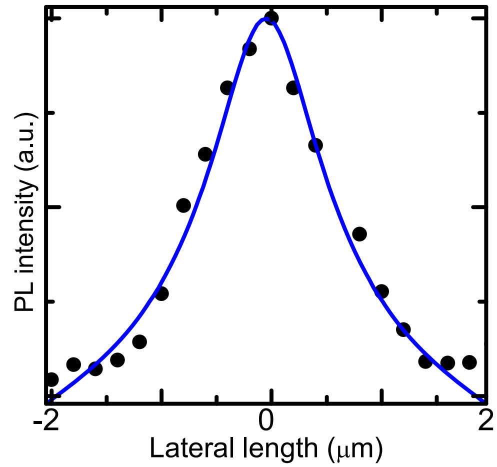


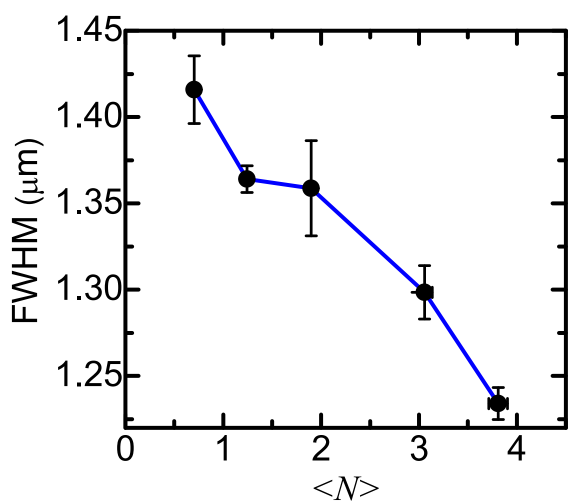
- 985.51 nm, 17.7 nm
- Fitted with a Lorentz function

- elongated PL image

PL Intensity Profile







- width > point spread function
- due to exciton diffusion

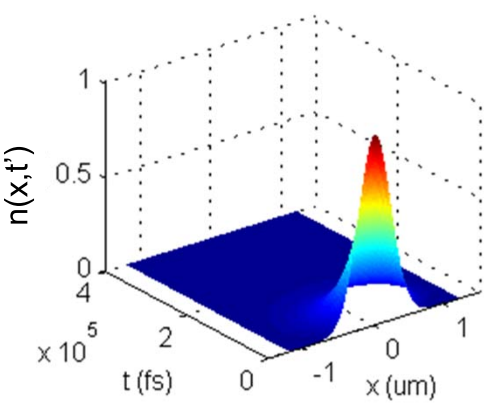
- Profile width changes with excitation power.

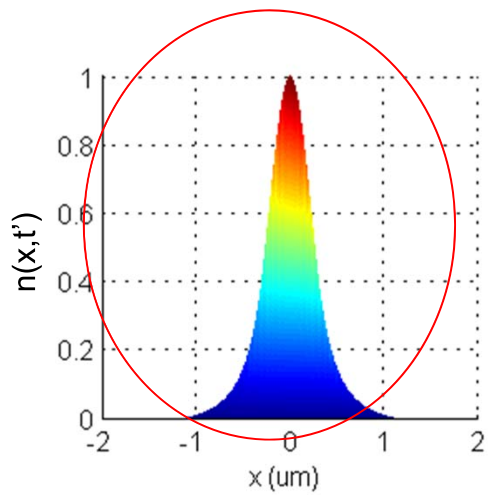
1D Diffusion Equation

$$\frac{\partial n(x,t')}{\partial t'} = -n(x,t') + L_D^2 \frac{\partial^2 n(x,t')}{\partial x^2} - C \cdot n(x,t')^2$$

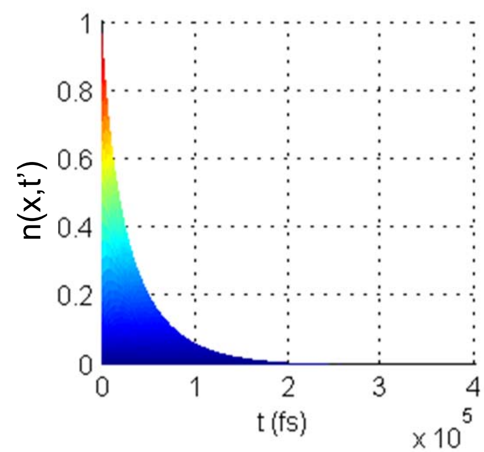
diffusion length

exciton-exciton
annihilation coefficient



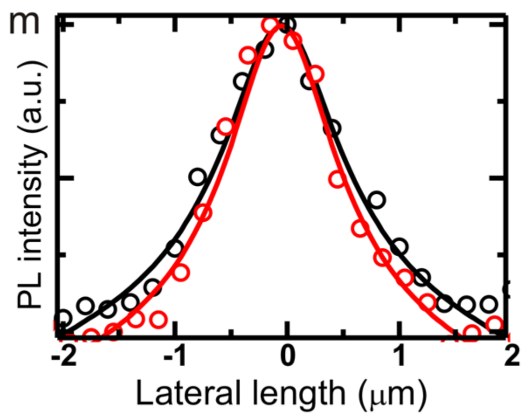


Intensity profile

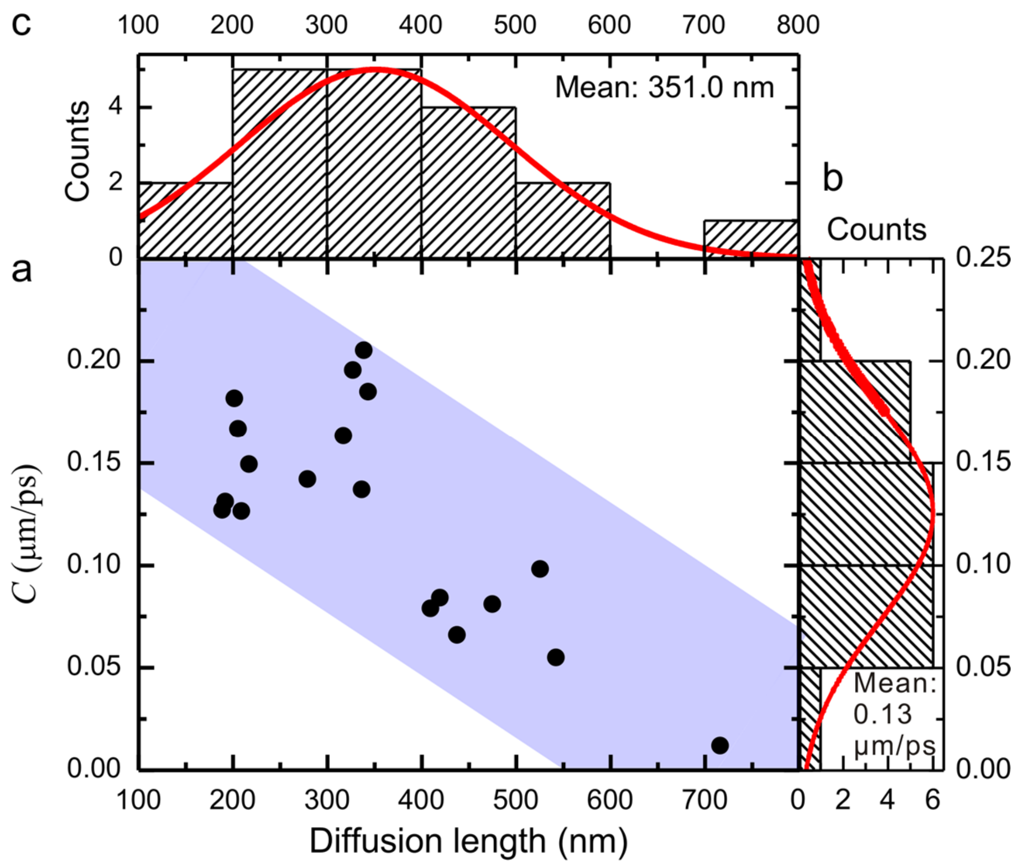


decay curve

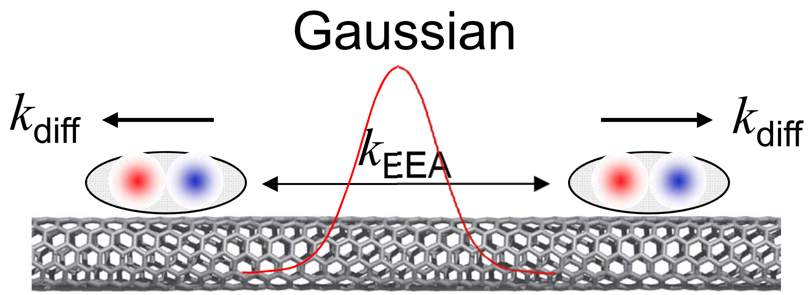
Fitting Intensity Profiles



- diffusion length L_D
- EEA coefficient C

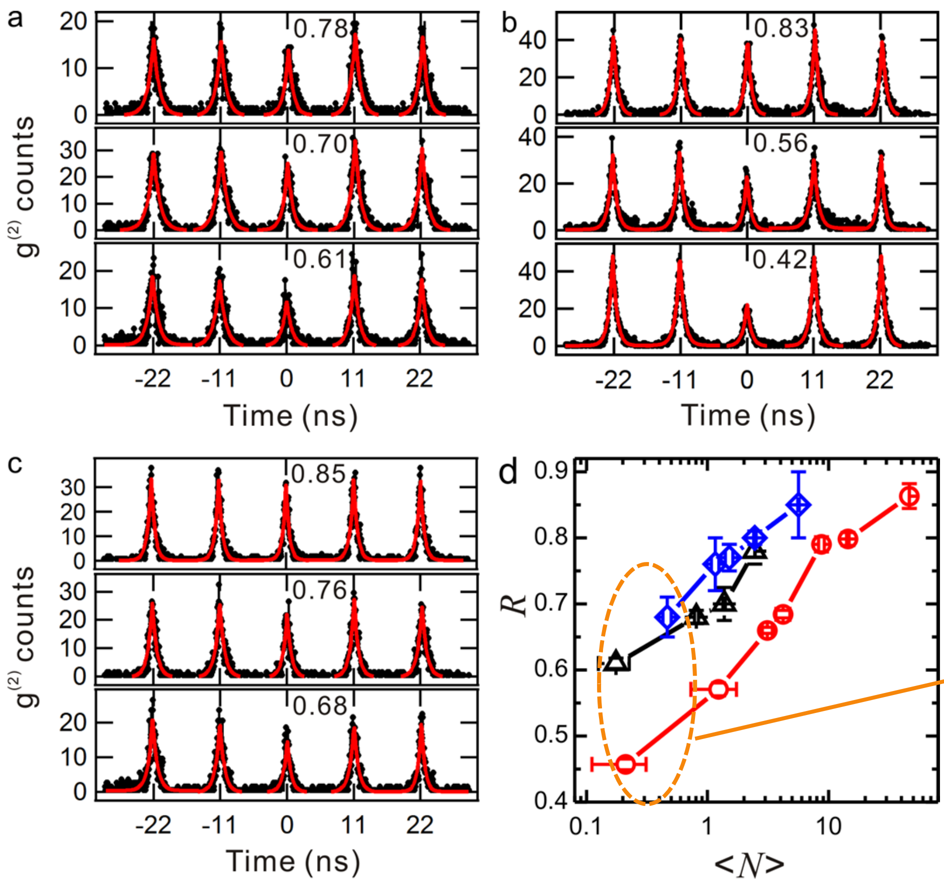


Exciton Diffusion ⇔ Exciton-Exciton Annihilation



- Larger diffusion length/rate
  → less efficient exciton-exciton annihilation
  → smaller C

Excitation Power Dependent $g^{(2)}$ Measurements



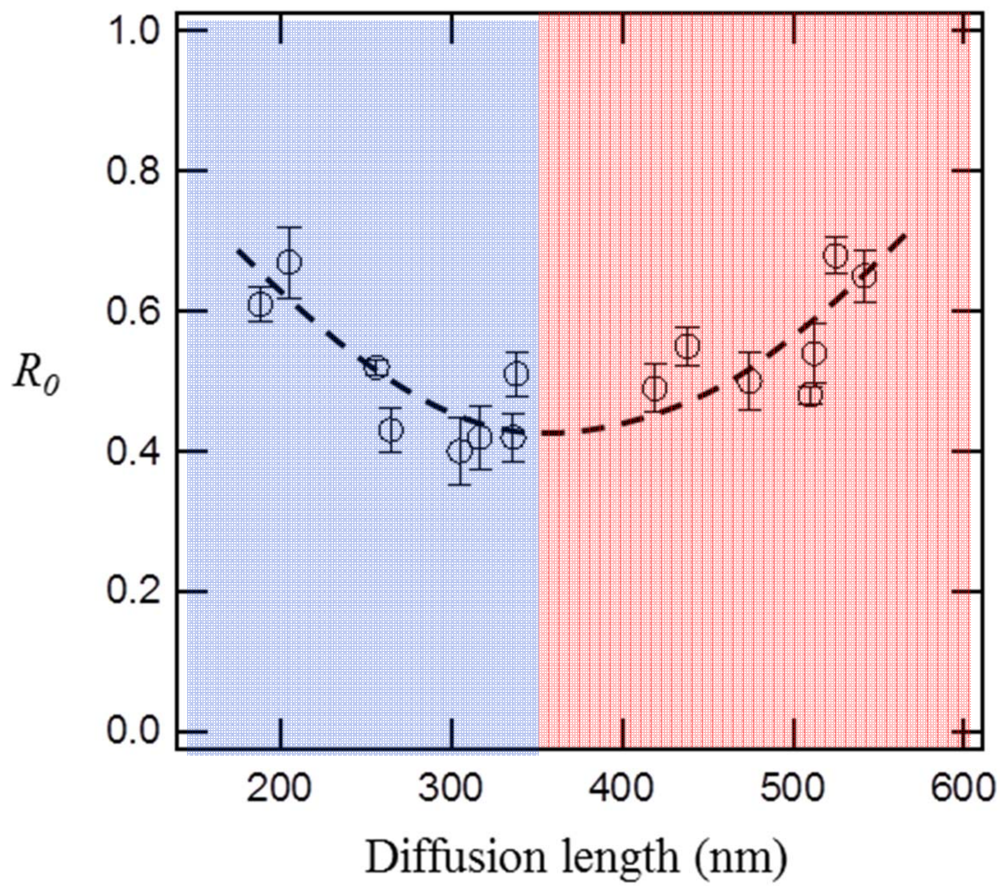
Area ratio:

$R = I_{center}/I_{side}$

minimum antibunching degree R_0

- R increases with increasing excitation power.

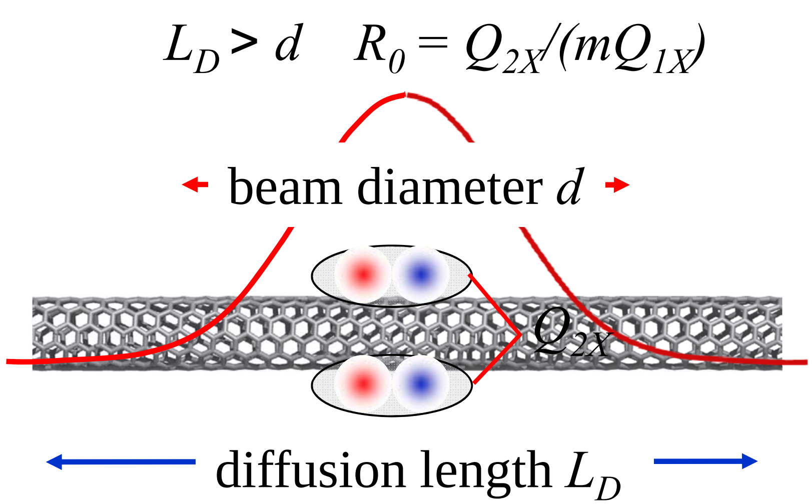
R_0 ⇔ diffusion length L_D

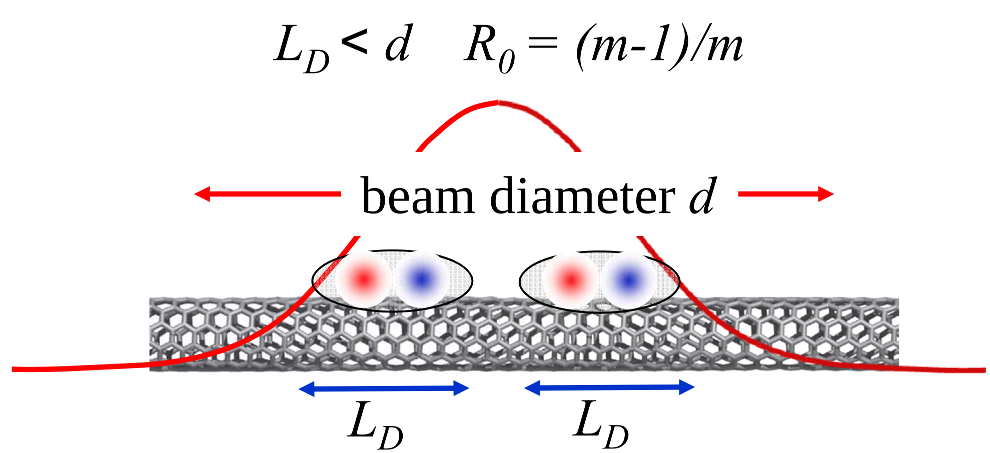


Minimum Antibunching Degree R_0

$$R_0 = Q_{2X} / (mQ_{1X}) + (m-1)/m$$

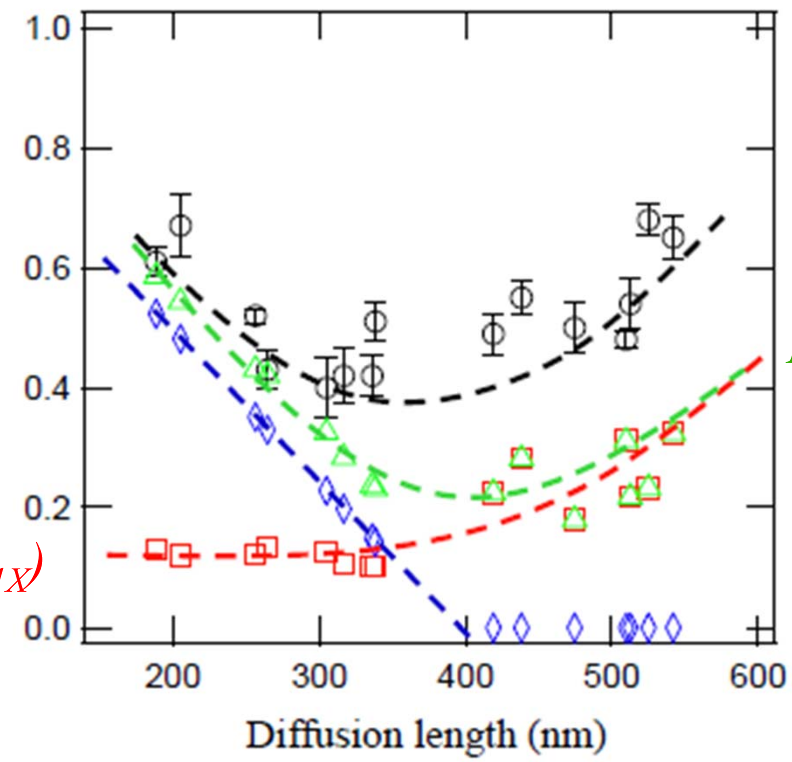
Q_{2X}: emission efficiency of two excitons
Q_{1X}: emission efficiency of one exciton
m: d/L_D





- Section of SWCNT behaviors like a QD.
- Excitons behave like independent emitters.

$R_0 \Leftrightarrow$ Diffusion Length L_D

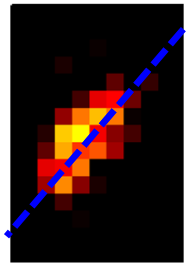


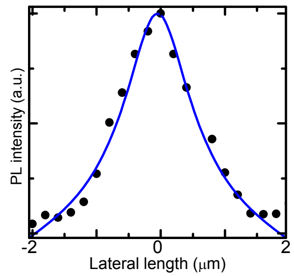
$R_0 = Q_{2X}/(mQ_{1X})+(m-1)/m$

$R_0 = Q_{2X}/(mQ_{1X})$

$R_0 = (m-1)/m$

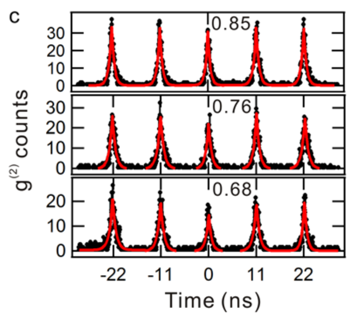
Summary

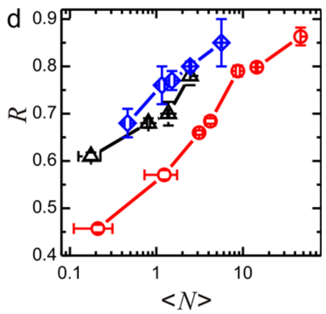




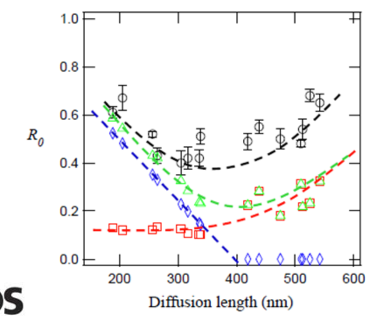
$$\frac{\partial n(x,t')}{\partial t'} = -n(x,t') + L_D^2 \frac{\partial^2 n(x,t')}{\partial x^2} - C \cdot n(x,t')^2$$

Diffusion length L_D and EEA coefficient C

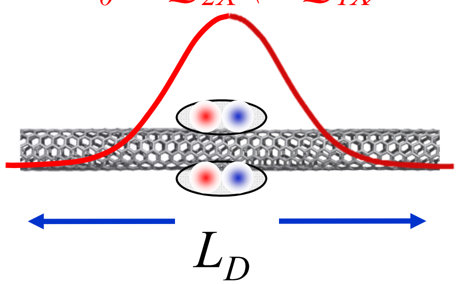




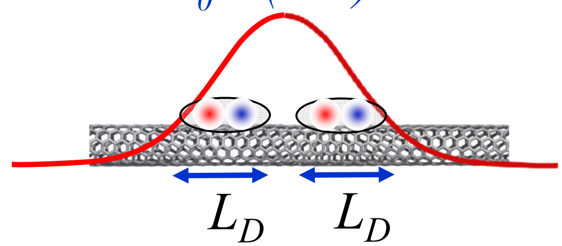
minimum antibunching degree R_0



$R_0 = Q_{2X}/(mQ_{1X})$



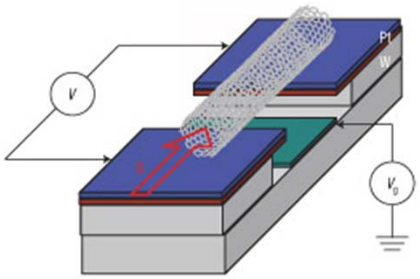
$R_0 = (m-1)/m$



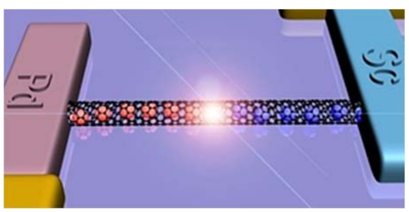
Oxygen Doping Modifies Excitonic Fine Structures of Carbon Nanotube

Ma et al. ACS Nano in submission

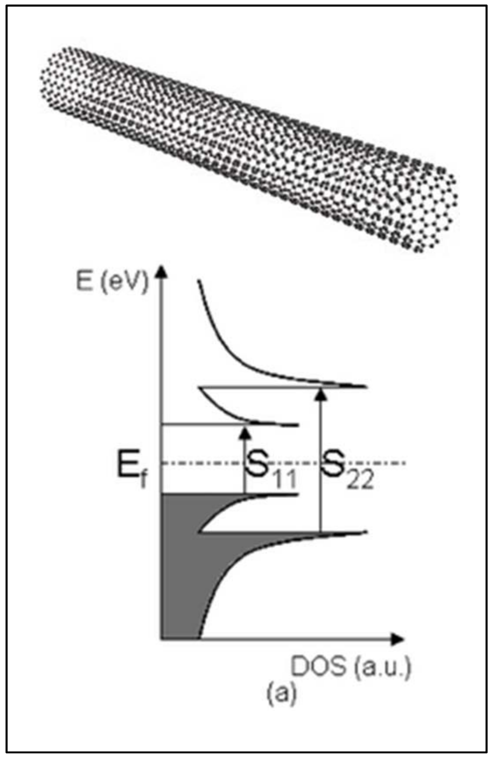
Photoluminescence of SWCNTs: Application

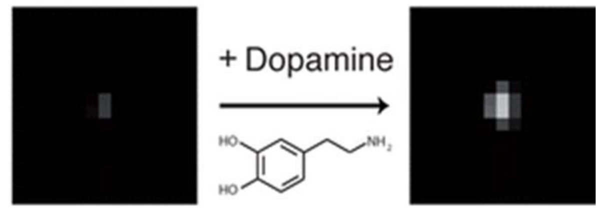


field-effect transistor
Cao et al. Nature Mater. 2005, 4

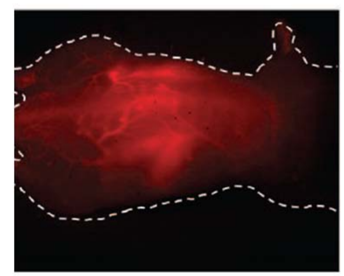


light emitting diode
Wang et al. Nano Lett. 2011, 11





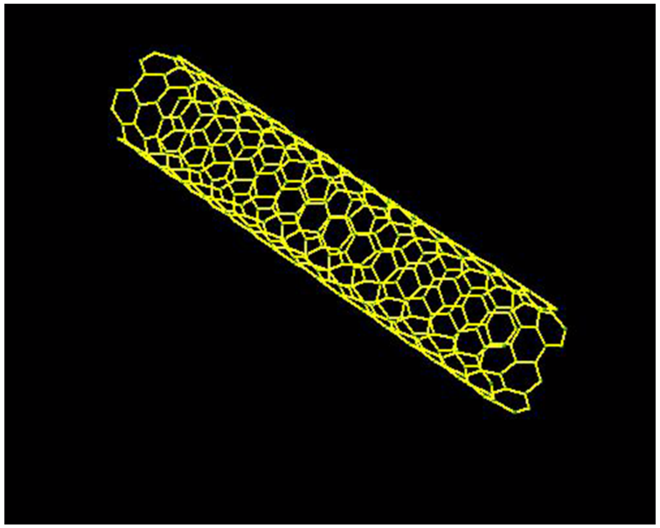
sensor
Kruss et al. J. Am. Chem. Soc. 2014



biological imaging
Welsher et al. Nature Nanotech. 2009

Photoluminescence of SWCNTs: Limitation

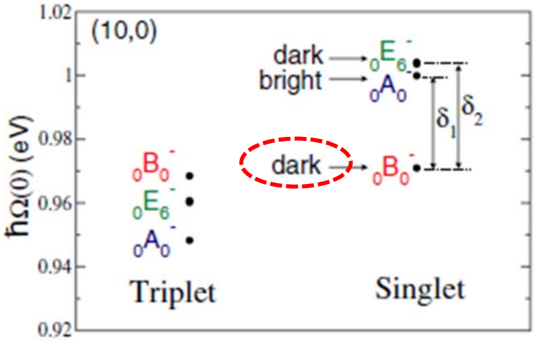
External factors



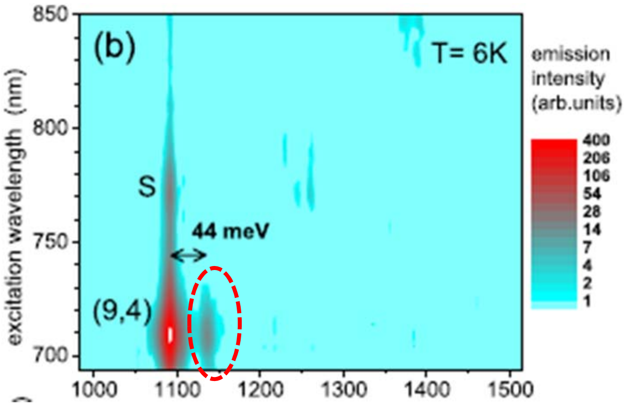
(S. Maruyama)

- single layer structure
- structural defects
- adsorbate molecules/atoms

Intrinsic factors



Spataru et al. Phys. Rev. Lett. 2005

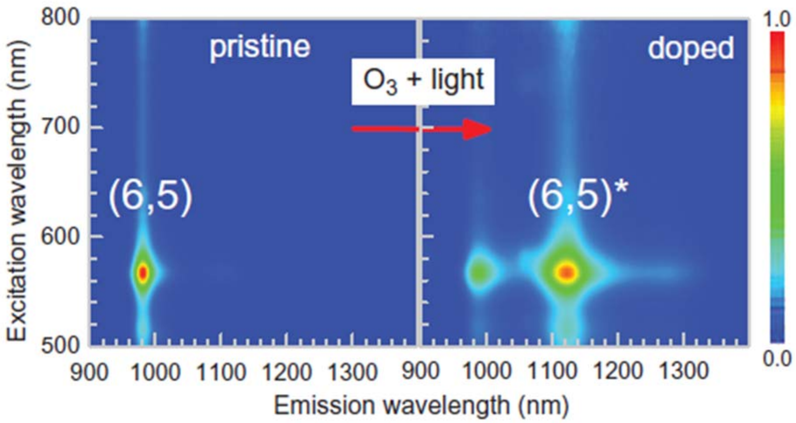


Kiowski et al. Phys. Rev. Lett. 2007

- dark states below the first bright state

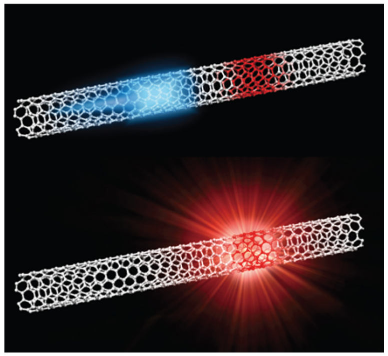
Controlled Doping of SWCNTs

oxygen doping



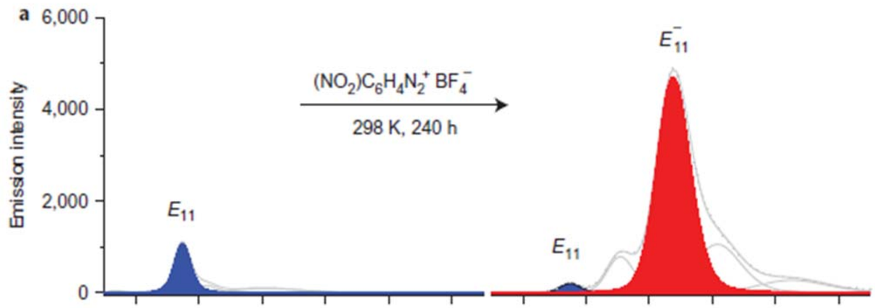
Ghosh et al. Science 2010

- additional bright, red-shifted peak



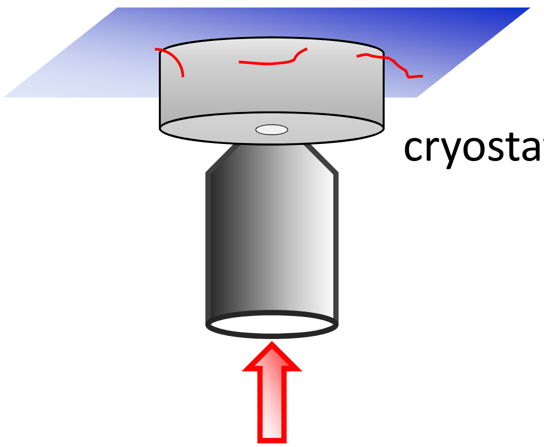
Miyauchi et al. Nature Photon. 2013

diazonium salt doping

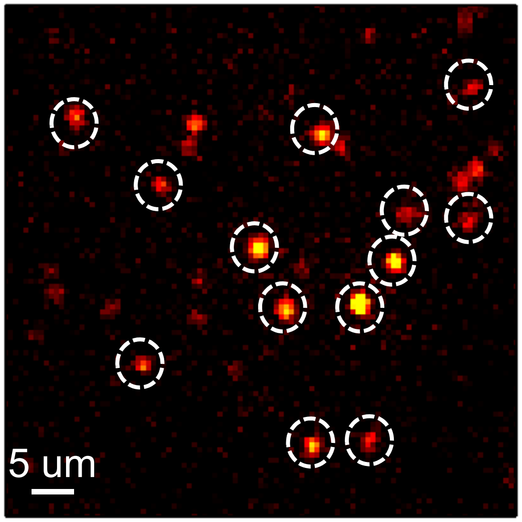


Piao et al. Nature Chem. 2013

Individual SWCNT Imaging at Low Temperature

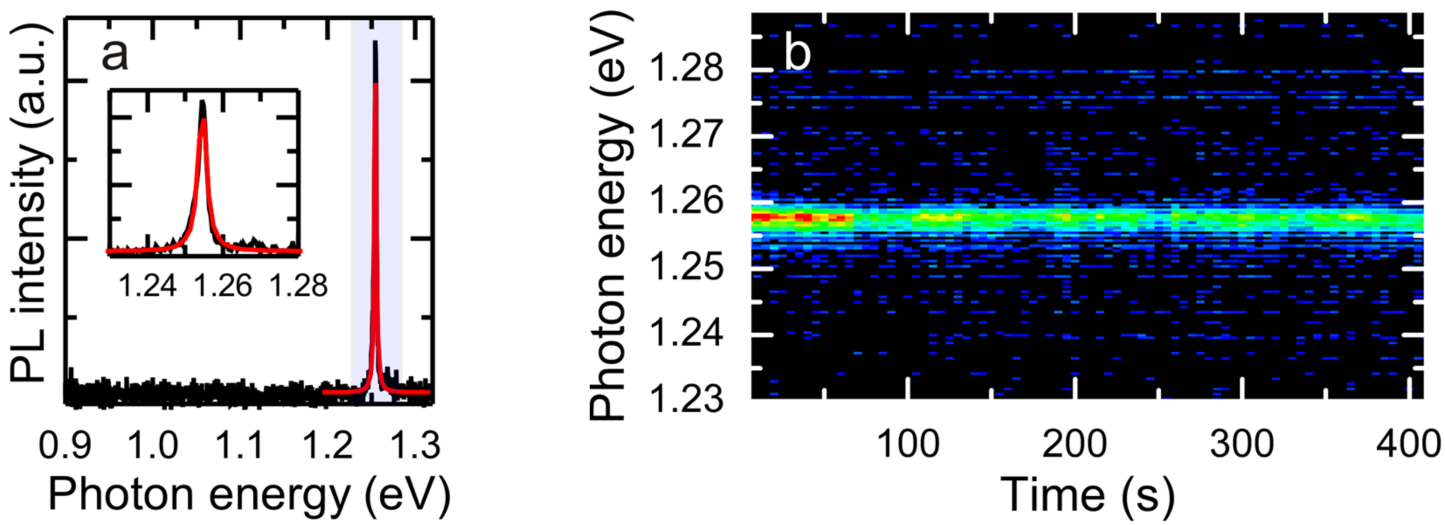


Wide field image



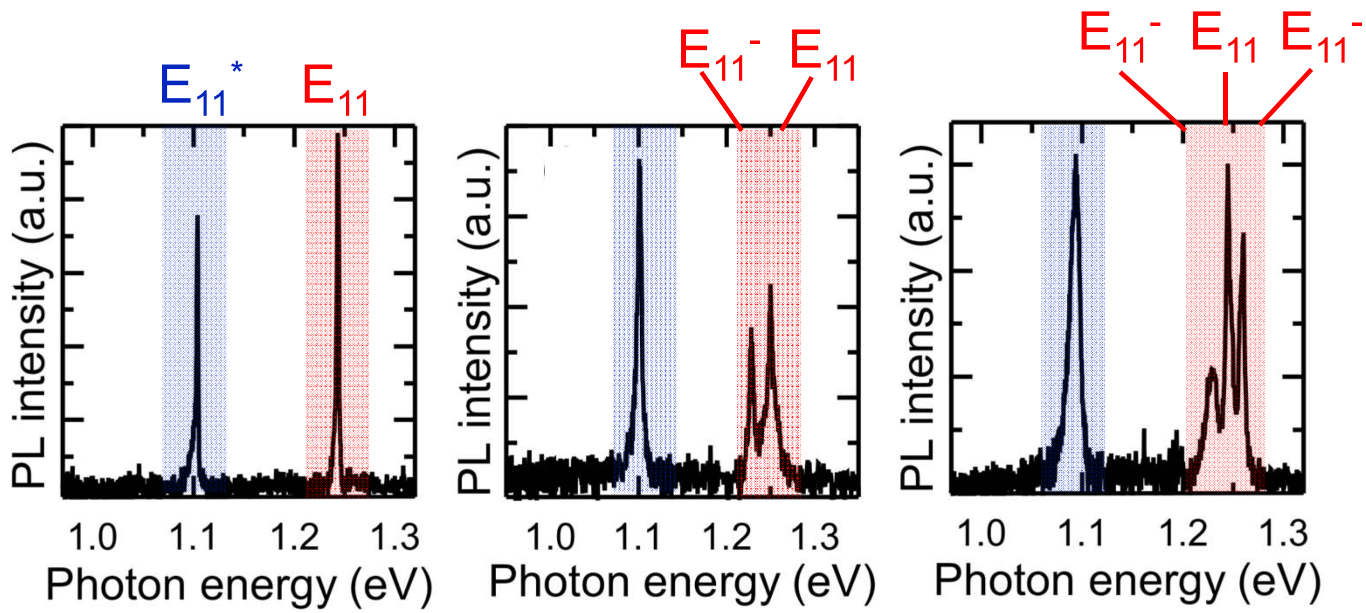
- diffraction-limited localized emission

Individual Pristine SWCNT



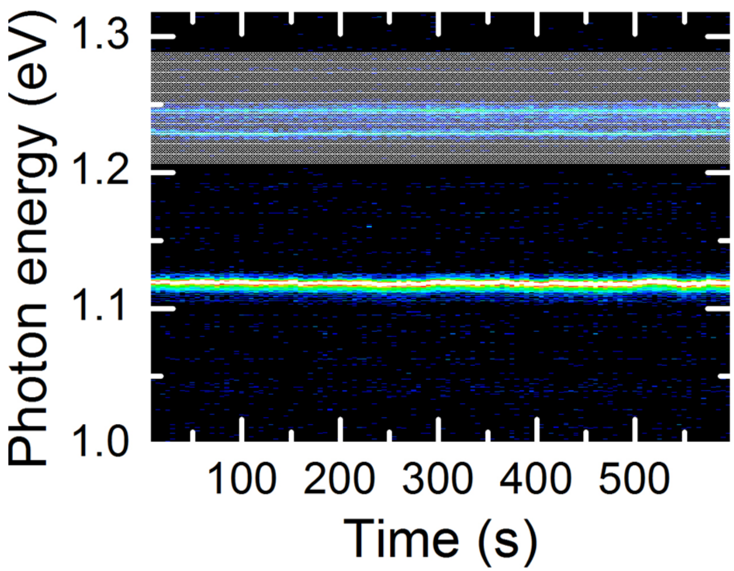
- individual symmetric (88%) peak at ~ 1.25 eV → E_{11}
- linewidth: 4.4 meV

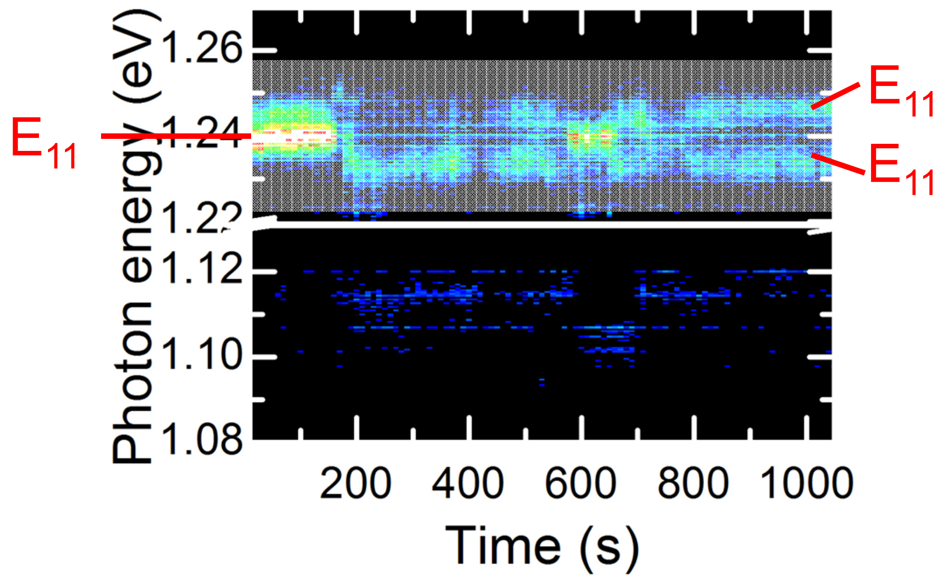
Individual Oxygen-Doped SWCNT



- spectral splitting of E_{11} peak → 2 to 3 peaks (70%)
- additional red-shifted peak → E_{11}^{*}

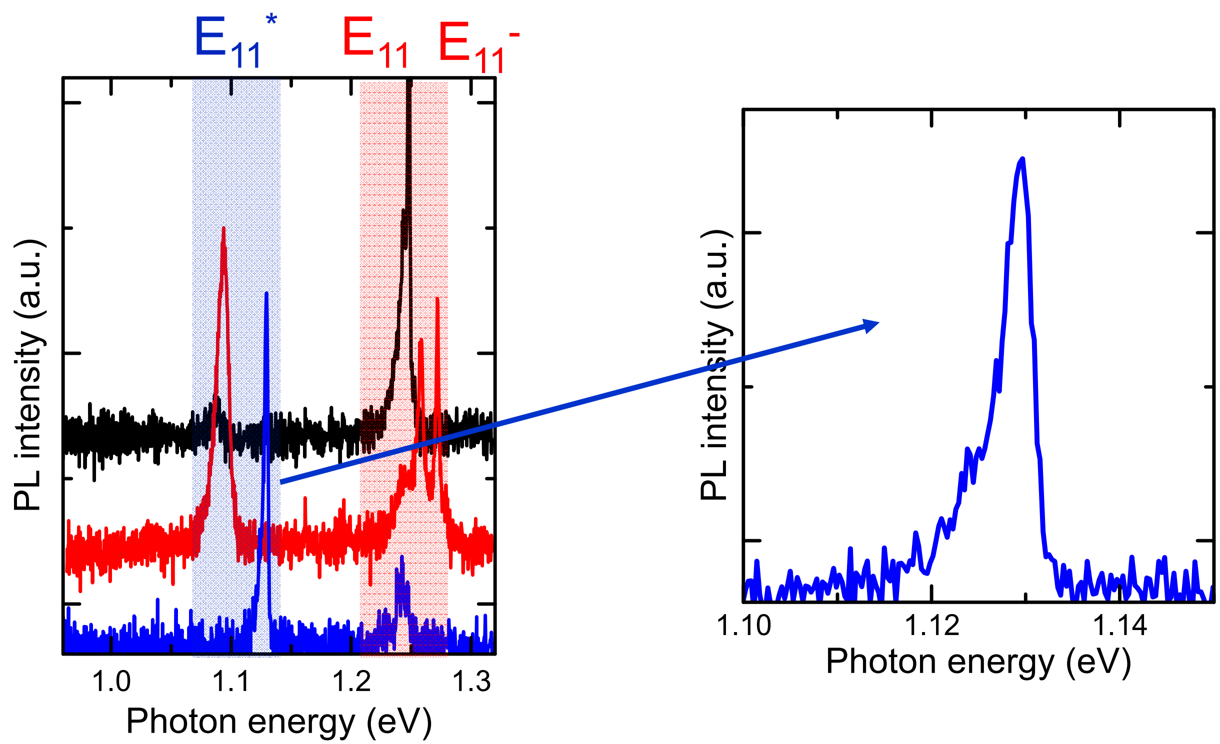
Time Evolution of E_{11} peak





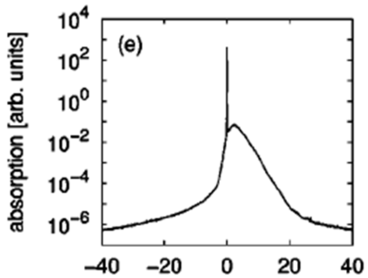
- stable peak position and intensity
- spectral splitting

Line Shape of E_{11}^* Peak

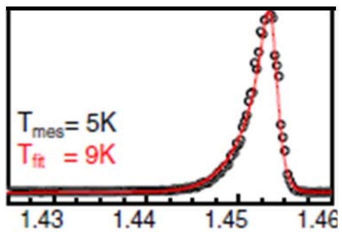


- asymmetric peak with long tail at the low energy side (83%)

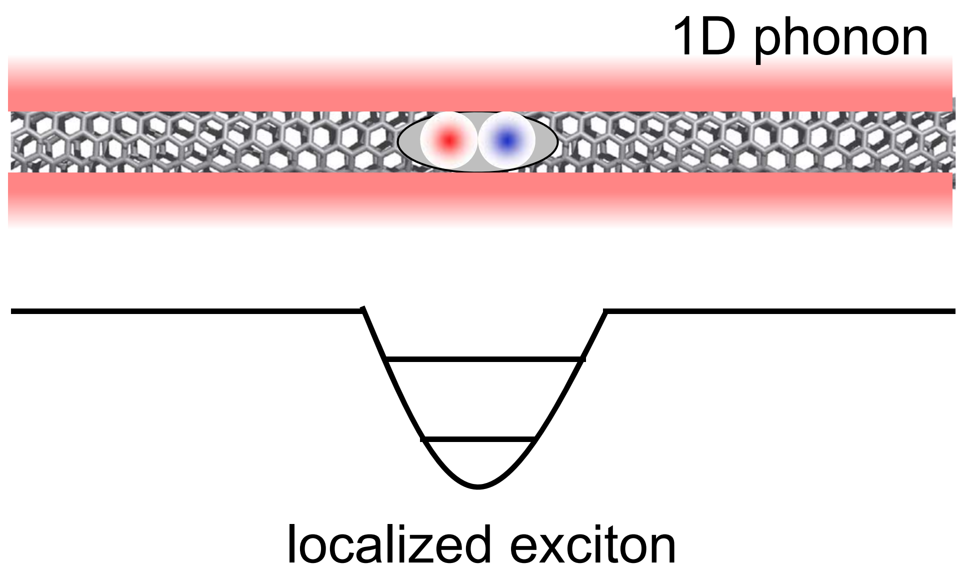
Line Shape of E_{11}^* Peak



Krummheuer et al. Phys. Rev. B 2002

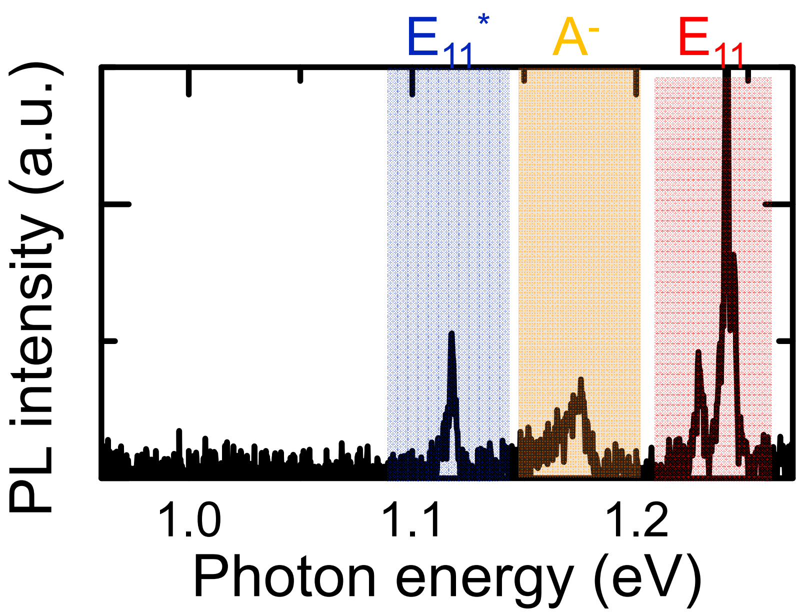


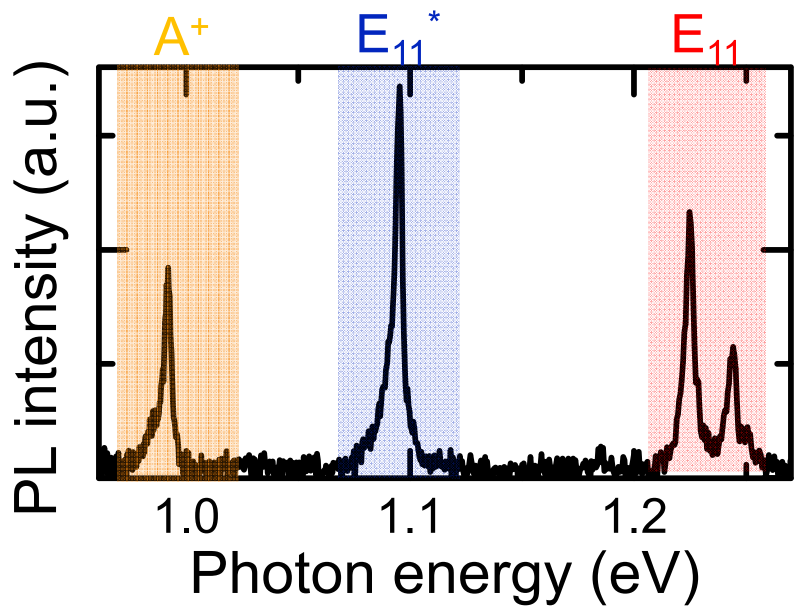
Galland et al. Phys. Rev. Lett. 2008



- due to coupling between localized exciton and 1D phonon
- E_{11}^* exciton is highly localized.

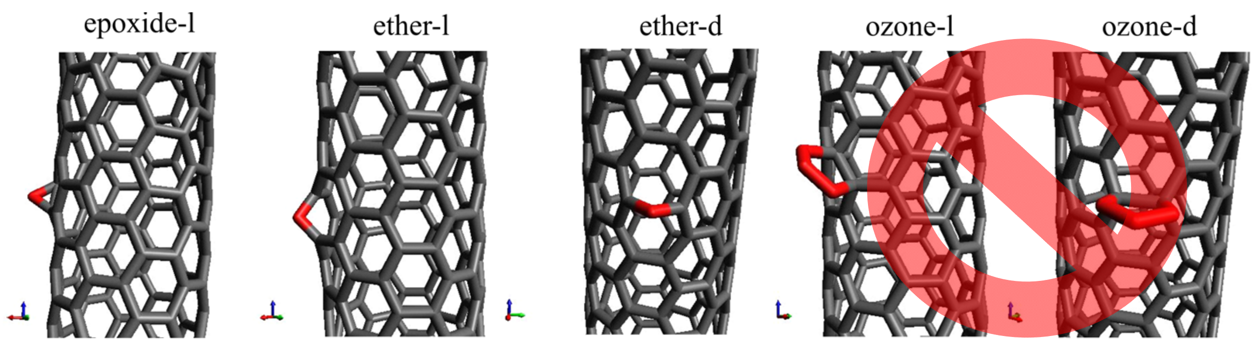
Additional Peaks





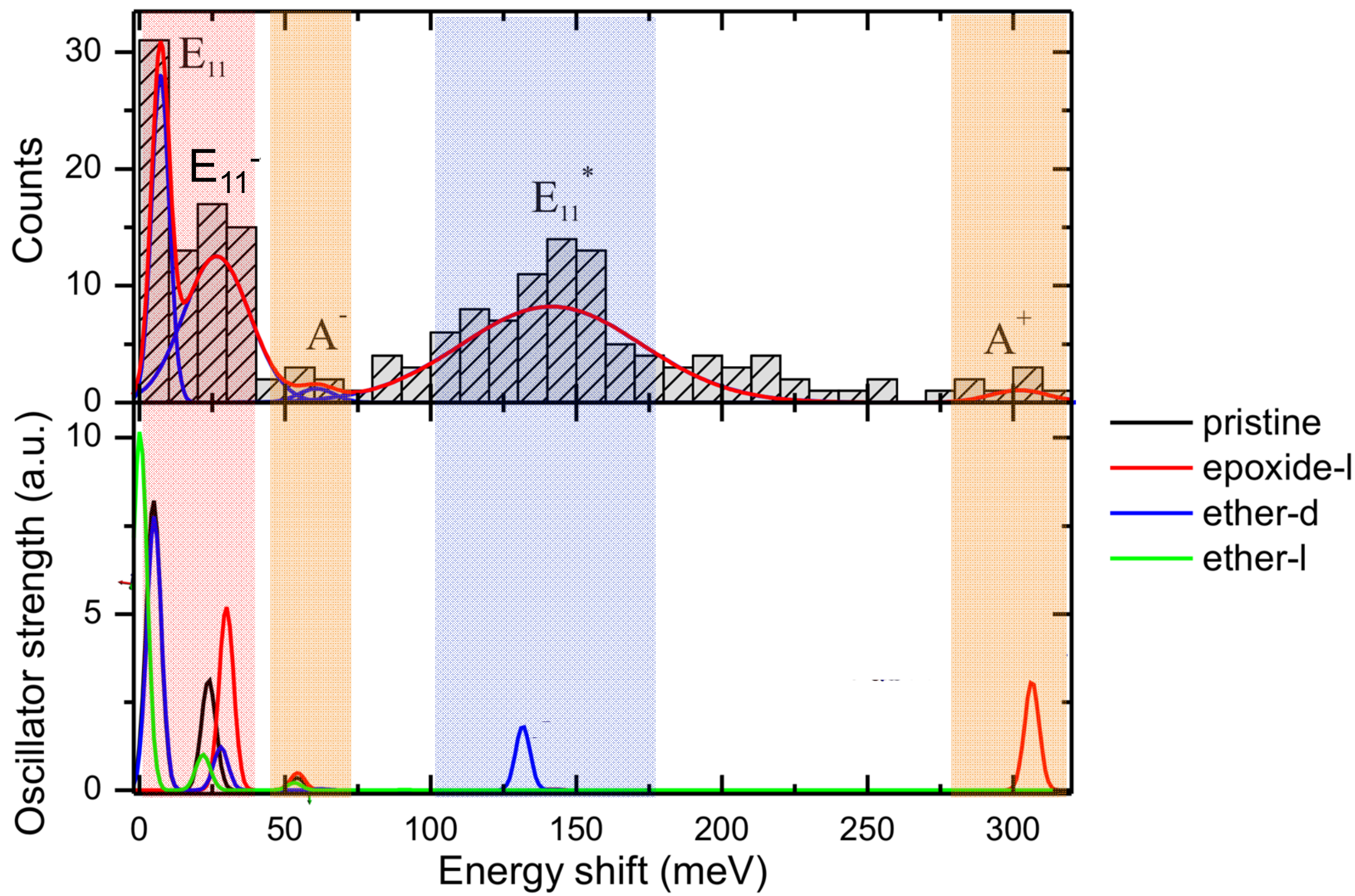
- Both A^{+} and A^{-} are asymmetric with long tail at the low energy side.
- A^{+} and A^{-} excitons are also localized.

Quantum Chemistry Computations

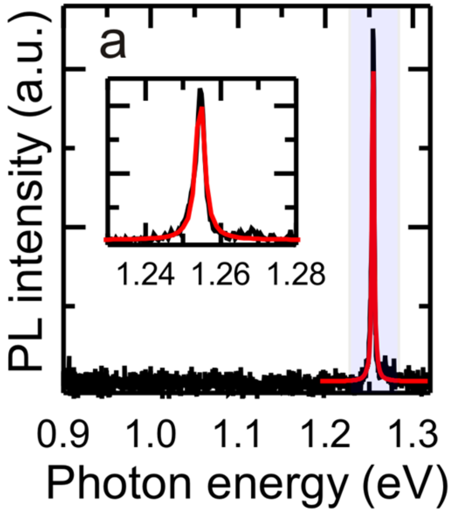


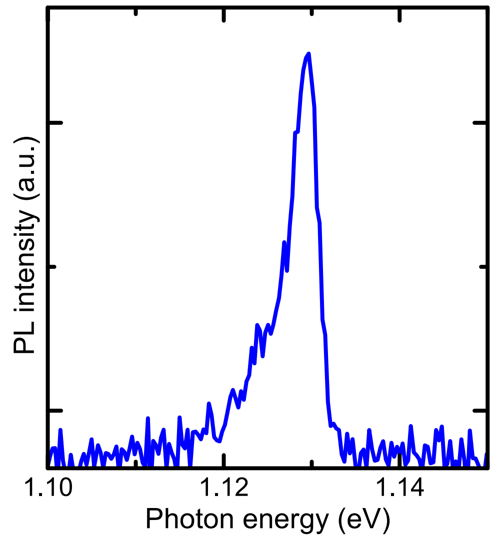
- Length of tube: 8 nm
- l: along tube axis; d: perpendicular to tube axis
- Geometry optimization: semi-empirical method (AM1 Hamiltonian, MOPAC program)
- Oscillator strengths and transition densities: Time-dependent Density Functional Theory (Gaussian 09, STO-3G basis set, B3LYP functional).

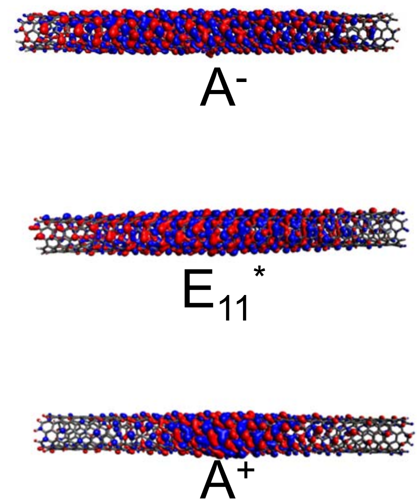
Comparison between Experiment and Simulation

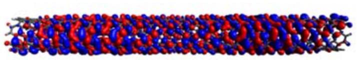


Exciton Transition Density







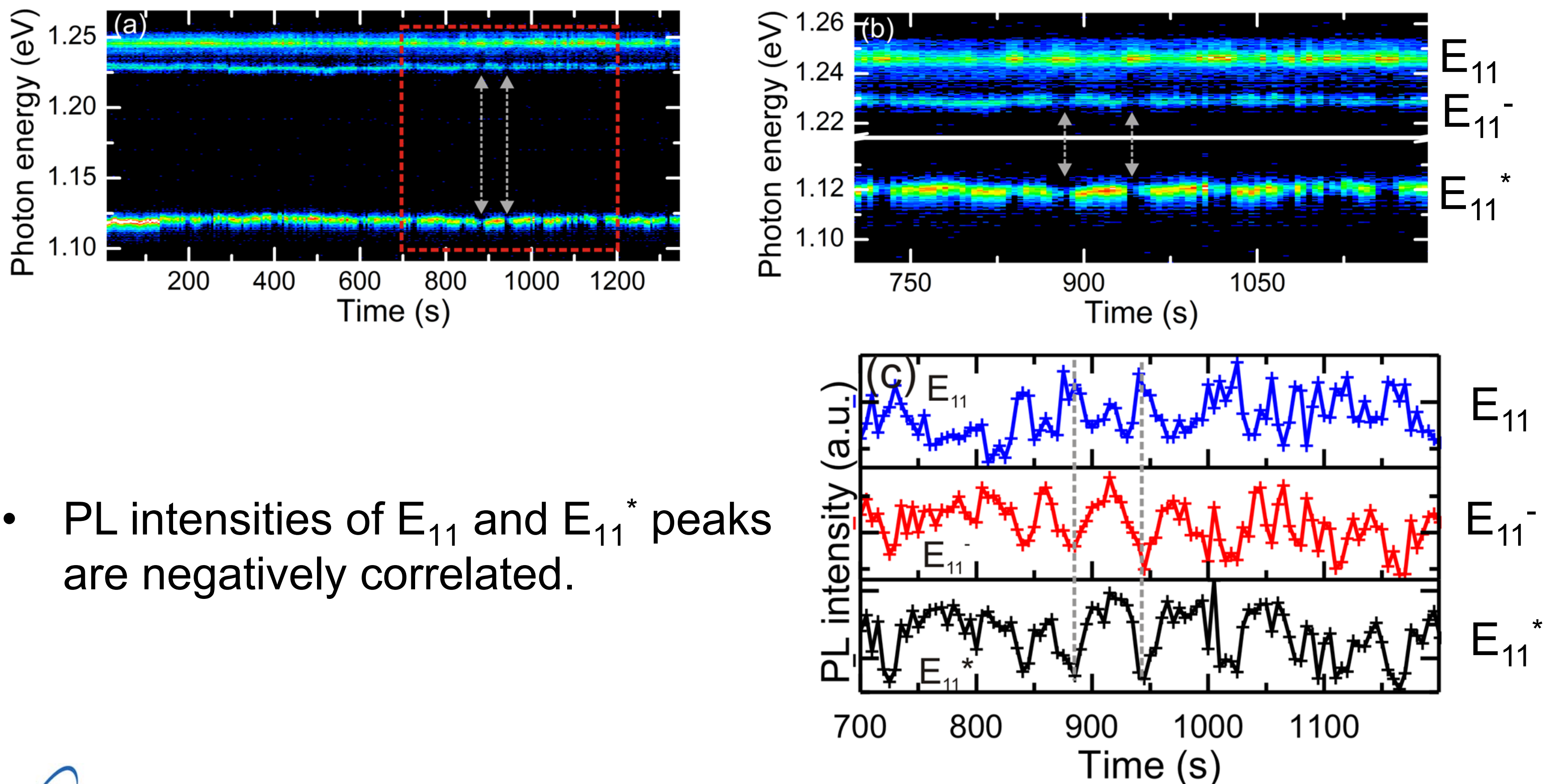


E_{11}

- symmetric lineshape
  → delocalized exciton

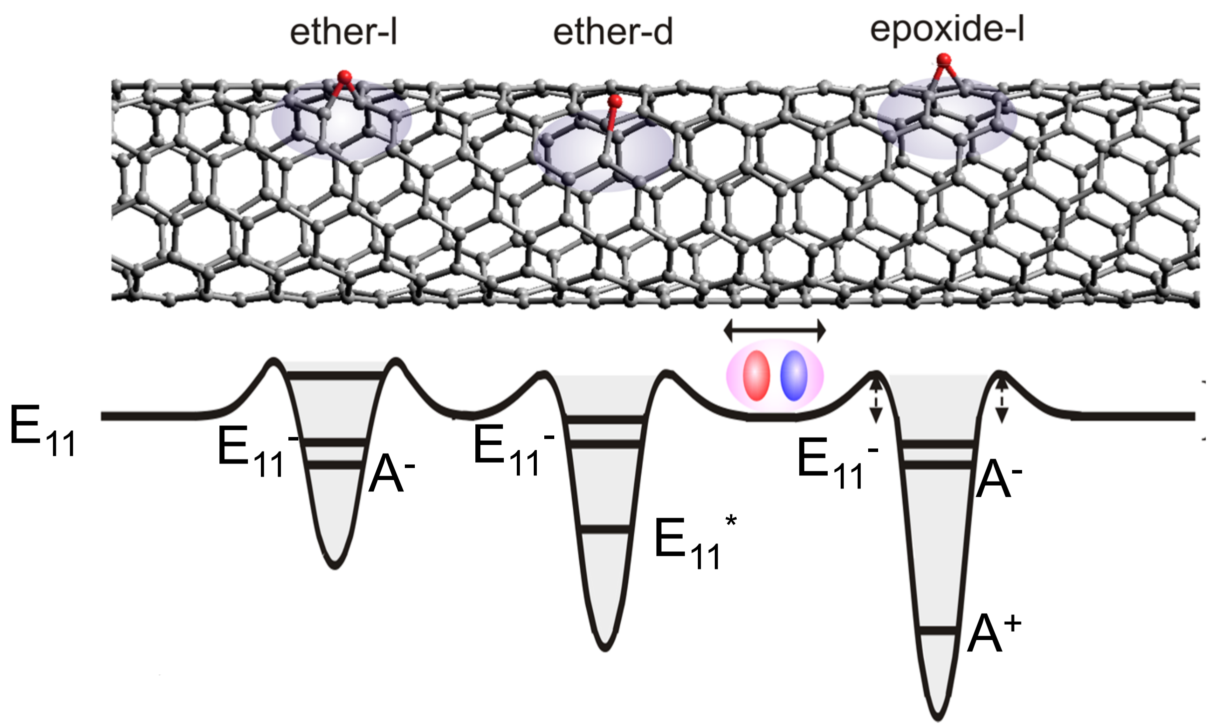
- asymmetric lineshape
  → localized exciton

Intensity Correlation between E_{11} and E_{11}^* peaks



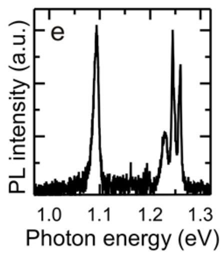
- PL intensities of E_{11} and E_{11}^* peaks are negatively correlated.

Excitonic Fine Structures

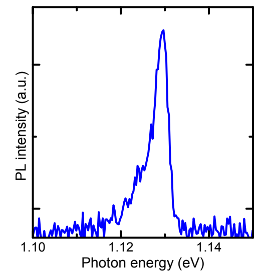


- Oxygen doping introduces potential wells localizing excitons.
- Potential fluctuation leads to negative intensity correlation between E_{11} and E_{11}^{*} peaks.

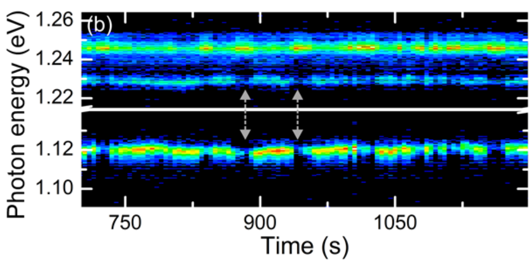
Summary



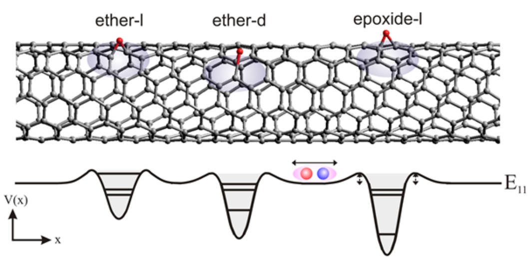
- spectral splitting of E_{11} peak



- asymmetric E_{11}^{*}, A^{+}, and A^{-} peaks



- negative intensity correlation between E_{11} and E_{11}^{*} peaks



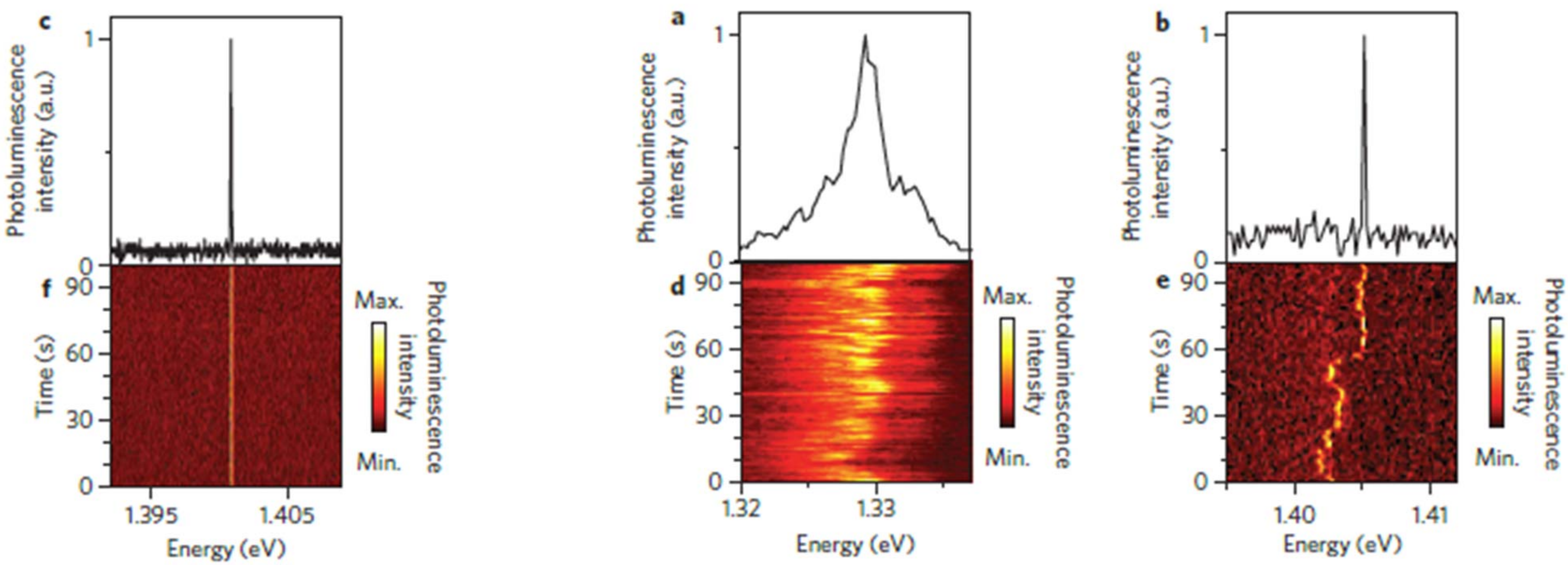
- excitonic fine structures of oxygen-doped SWCNTs

Influence of Exciton Dimensionality on Spectral Diffusion of Single-Walled Carbon Nanotubes

Ma et al. ACS Nano in submission

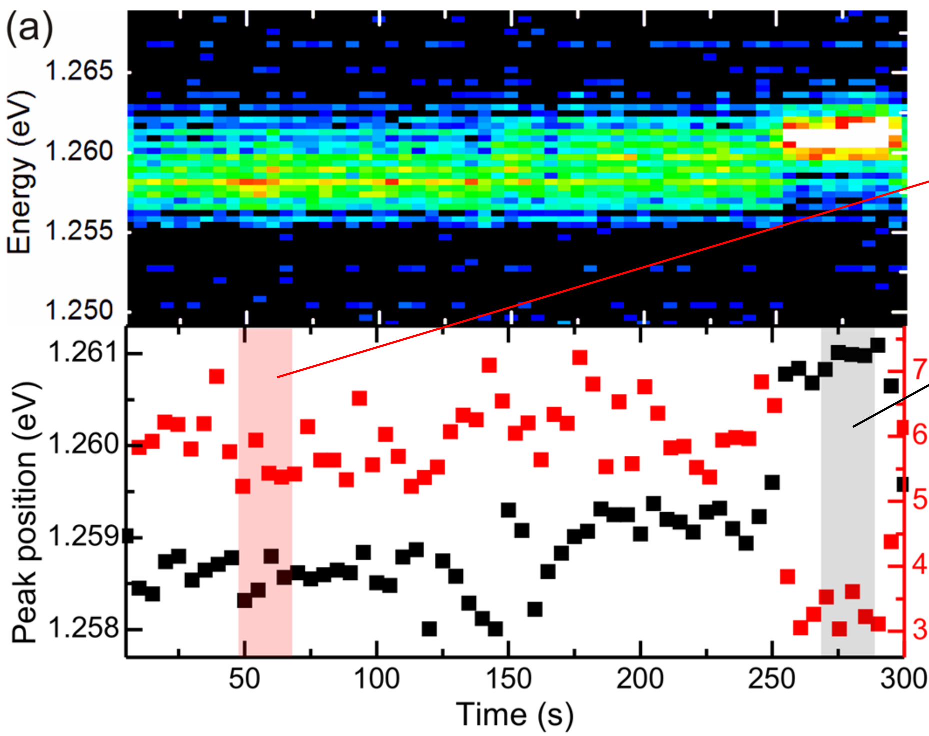
Spectral Diffusion of SWCNTs

Ideal spectra | Real spectra

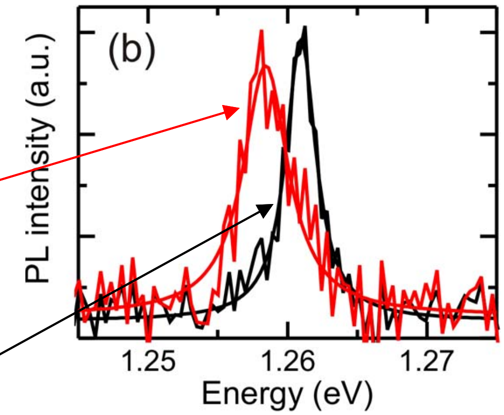


- Quantum information processing requires spectral-diffusion free emission → physical mechanism behind spectral diffusion

PL spectra of Individual SWCNTs at 4K

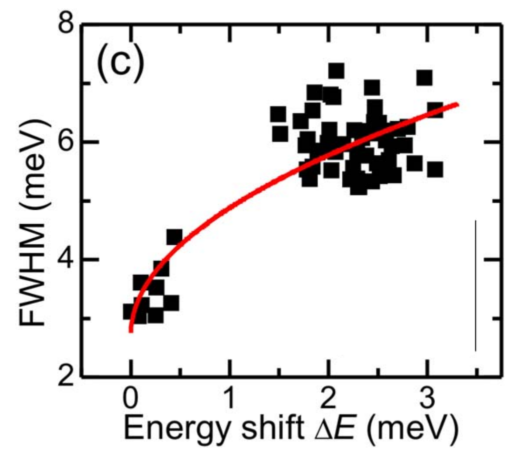


5s per each spectrum



red-shift

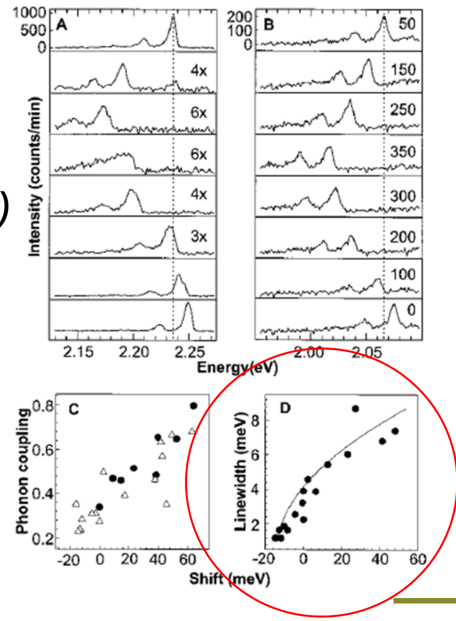
broader spectrum

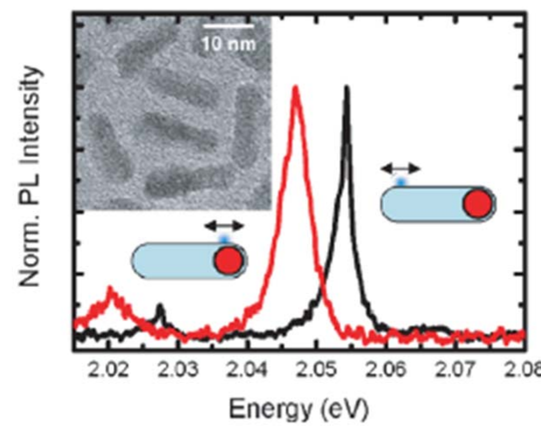


sub-linear correlation

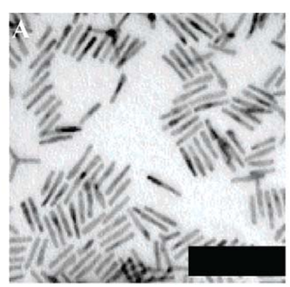
Quantum-confined Stark effect (QCSE)

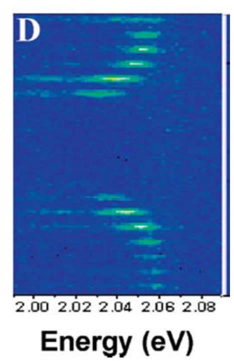
CdSe QDs
(Bawendi, Science 97)





CdSe/CdS nanorods
(Weller, PRL 2004)

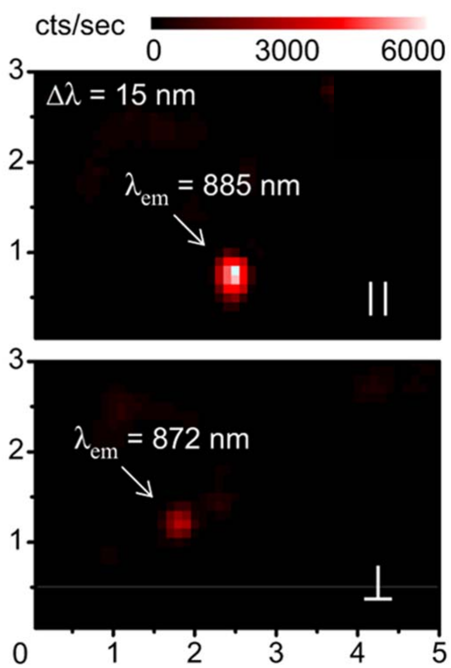


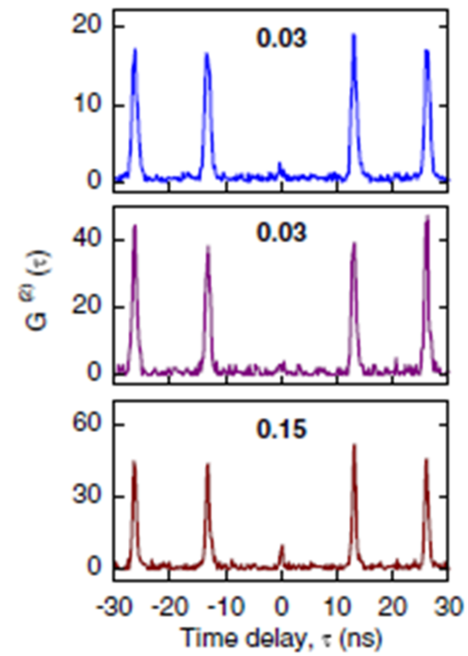


CdSe/ZnS nanorods
(Banin, Nano Lett. 2005)

SWCNTs at Cryogenic Temperature

4 K





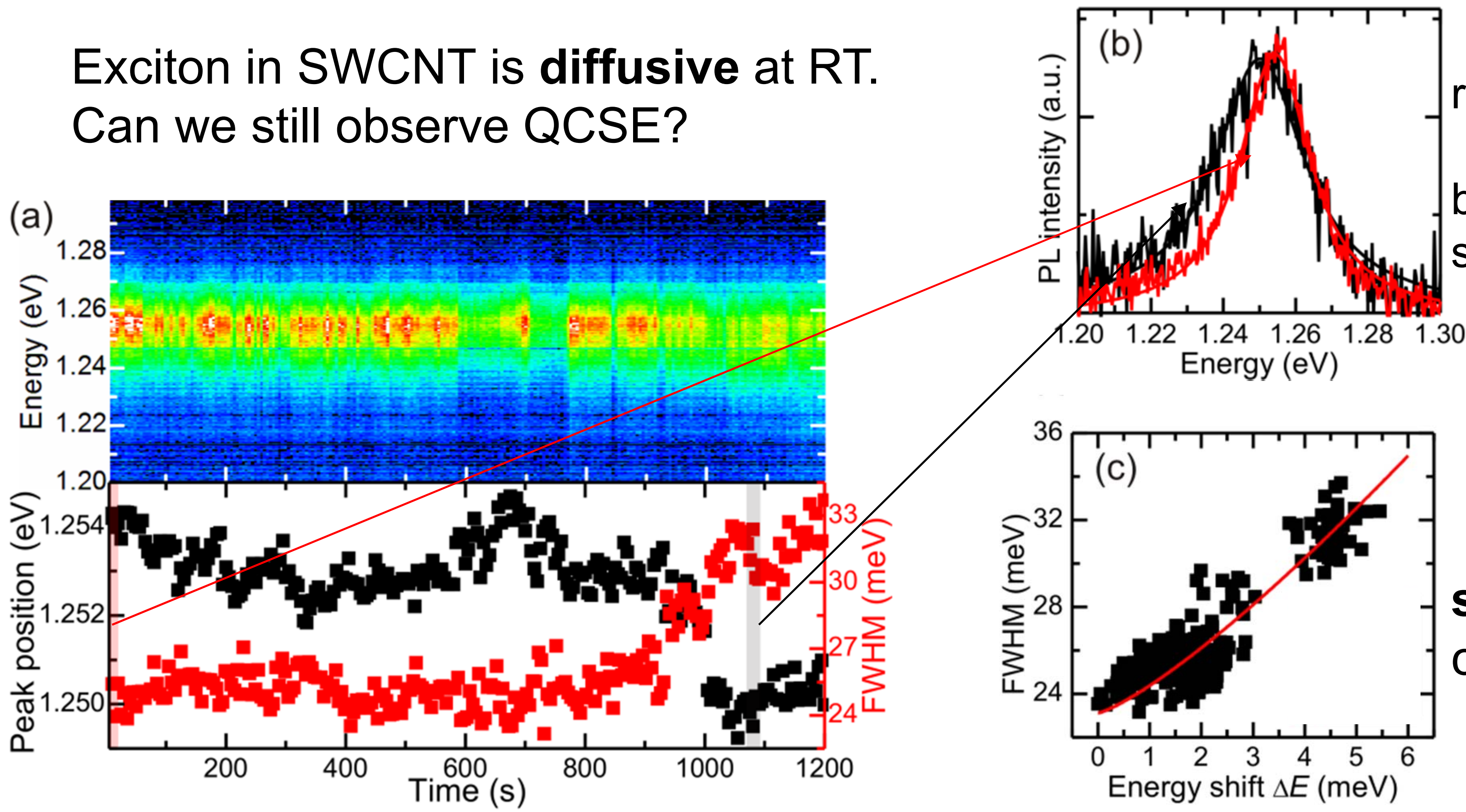
localized emission complete antibunching

Hoegele et al. Phys. Rev. Lett. 2008

- Excitons in SWCNTs at 4K is localized to **QD-like** excitonic states.
  → sublinear correlation between linewidth and peak shift.

PL spectra of Individual SWCNTs at RT

Exciton in SWCNT is **diffusive** at RT.
Can we still observe QCSE?



red-shift

broader spectrum

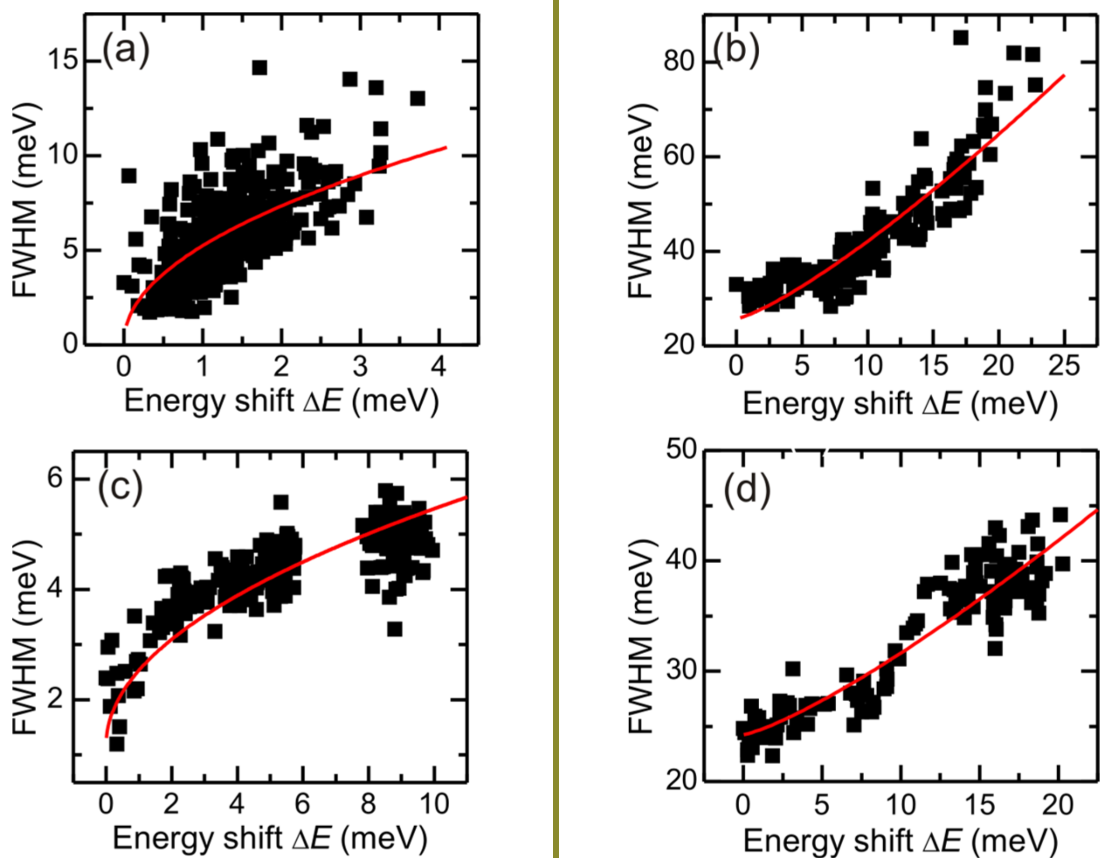
super-linear correlation

Exciton Dimensionality ↔ Correlation Coefficient

4K
exciton 0D

↕

sublinear
correlation

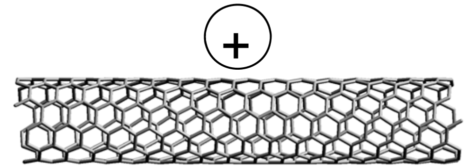


RT
exciton 1D

↕

Superlinear
correlation

Single Point Charge Model



For a SWCNT at low electric field, an energy shift of the binding energy (ΔE) caused by QCSE can be described by:

$$\Delta E = k_{\mathrm{b}} \frac{(edF)^2}{E}$$

e: electron charge d: tube diameter
E: tube binding energy at zero field
F: electric field induced by surface charges
k_{b}: constant

If we use a Gaussian stochastic model to describe spectral diffusion behavior:

$$\left\langle \delta(\Delta E)(t)\delta(\Delta E)(0) \right\rangle = \sigma^2 e^{-t/t_c}$$

σ : spectral broadening in meV

At time $t=0$ we obtain

$$\left\langle \delta^2(\Delta E)(0) \right\rangle = \sigma^2$$

In a simple assumption, we assume that there is an external point charge located on the surface of a SWCNT that creates a local electric field:

$$F = \frac{q}{4\pi\varepsilon r^2}$$

ε: permittivity of the surrounding environment
r: exciton-charge distance

Single Point Charge Model

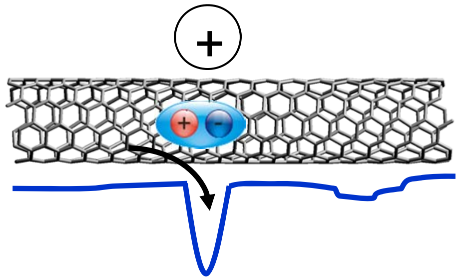
At cryogenic temperature:

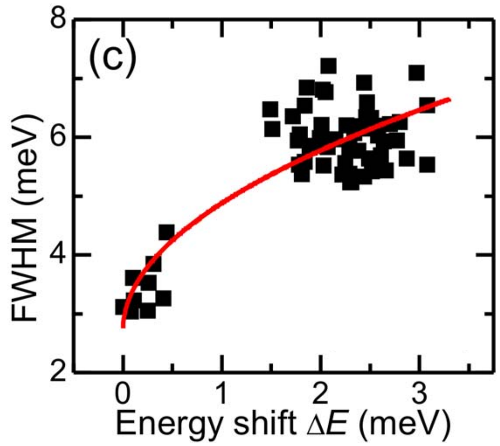
- Excitons are localized to quantum-dot-like states.
- Exciton-charge distance r and local environment permittivity ε: constants.
- Exciton binding energy fluctuation is mainly induced by fluctuations in surface charges:

$$\delta F = \frac{1}{4\pi\varepsilon r^2}\delta q$$

$$\Downarrow$$

$$\sigma \propto \sqrt{\Delta E}$$

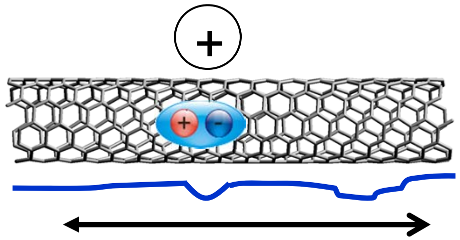




Single Point Charge Model

At room temperature:

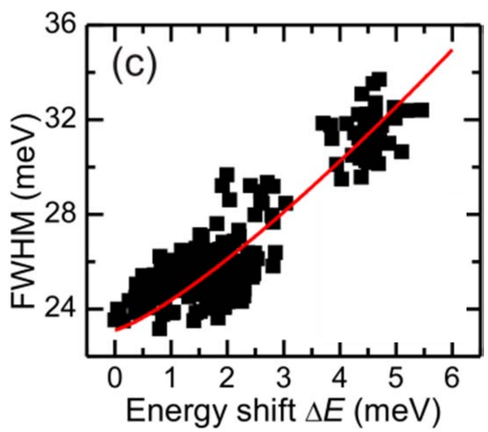
- Excitons are diffusive (~100 nm).
- Large fluctuation in exciton-charge distance r.
- Contributions of surface charge/dielectric environment fluctuation become negligible.



$$\delta F = -\frac{2q}{4\pi\varepsilon r^3}\delta r$$

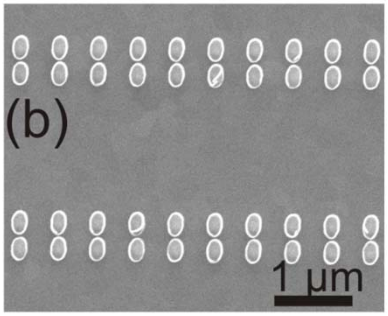
$$\Downarrow$$

$$\sigma \propto \Delta E^{5/4}$$

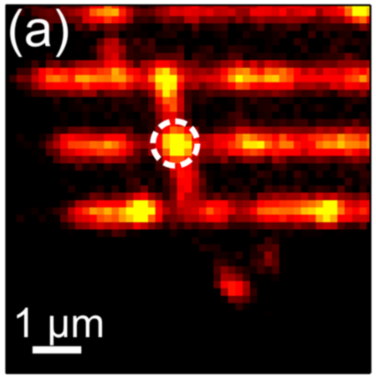


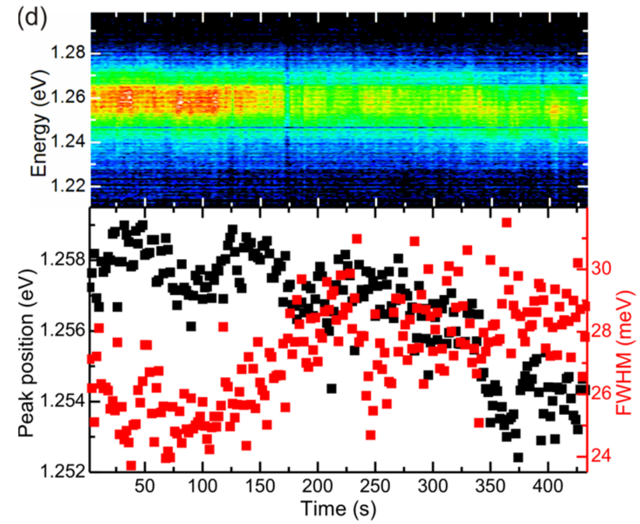
SWCNTs Coupled to Surface Plasmons

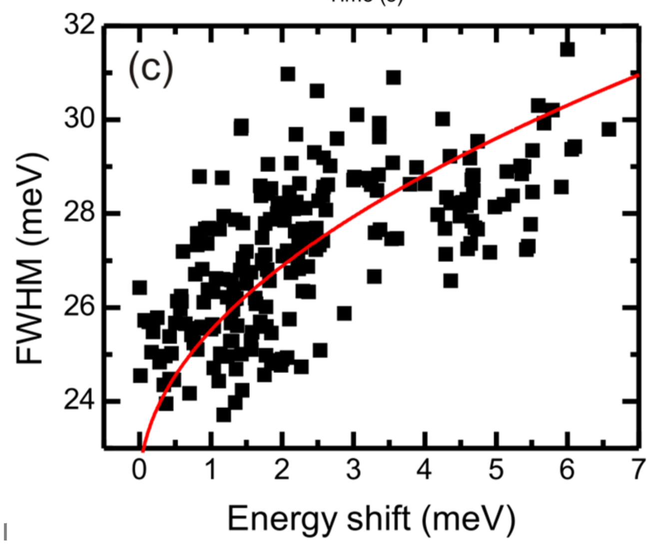
SEM



PL image





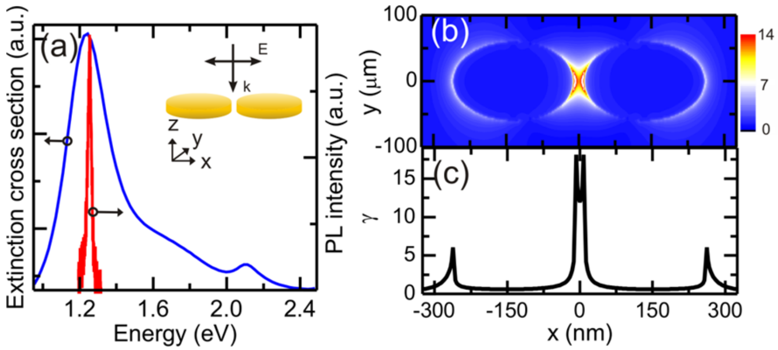


$$\sigma \propto \sqrt{\Delta E}$$

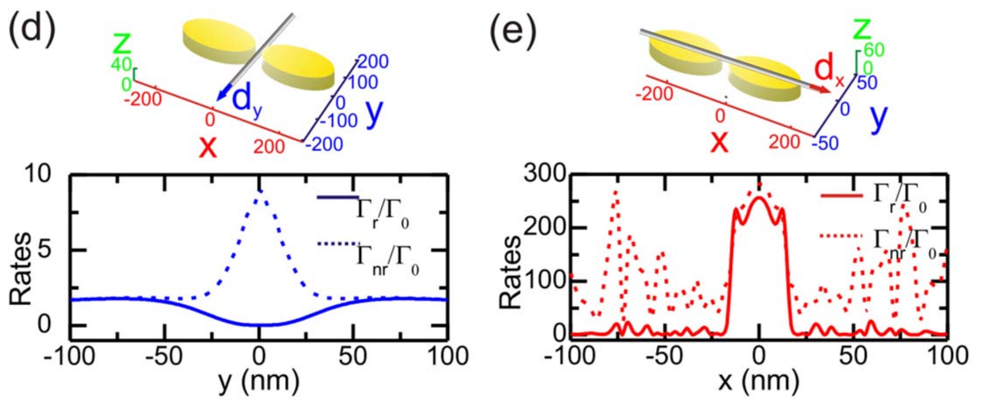
⬇

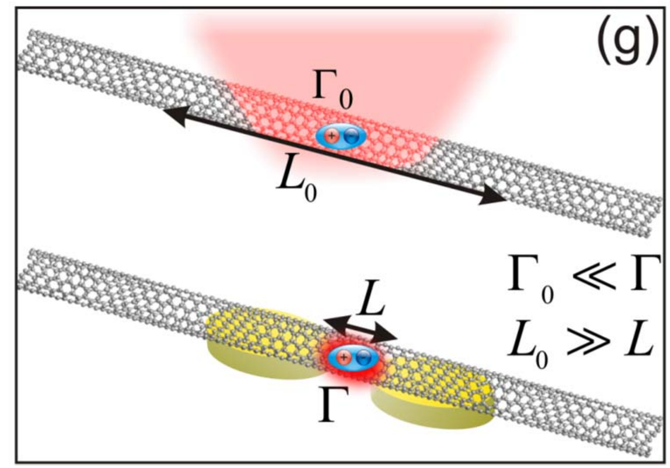
exciton “localization”
at room temperature

Numerical Simulations



- highly confined excitation regine (<30nm)

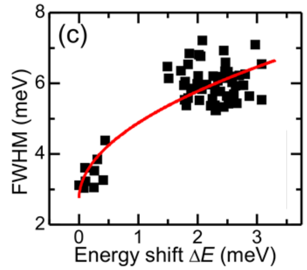




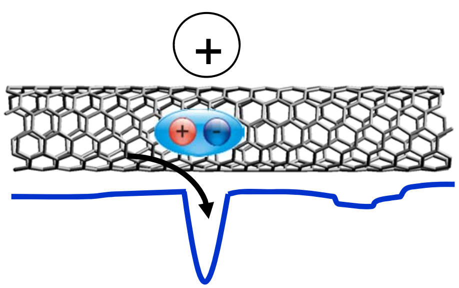
- strongly enhanced decay rates in the gap → chance of exciton diffusion greatly decreased.

Summary

4K

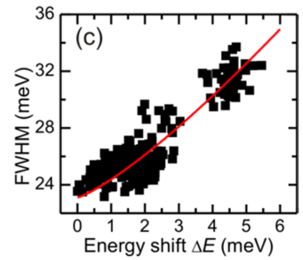


$$\sigma \propto \sqrt{\Delta E}$$

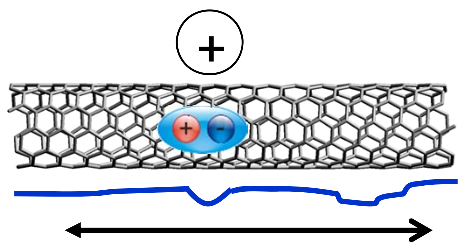


exciton: 0D

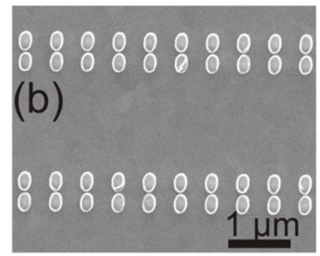
RT

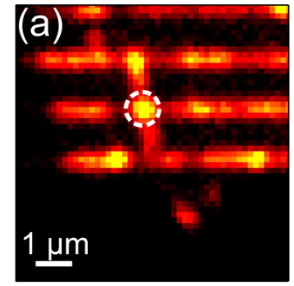


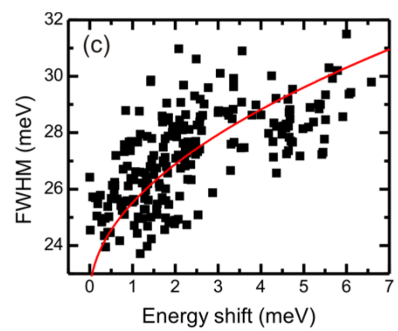
$$\sigma \propto \Delta E^{5/4}$$



exciton: 1D

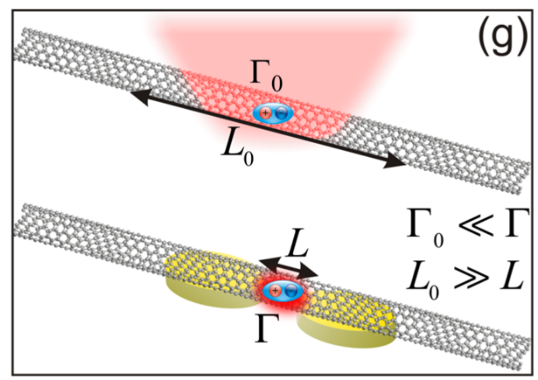






$$\sigma \propto \sqrt{\Delta E}$$

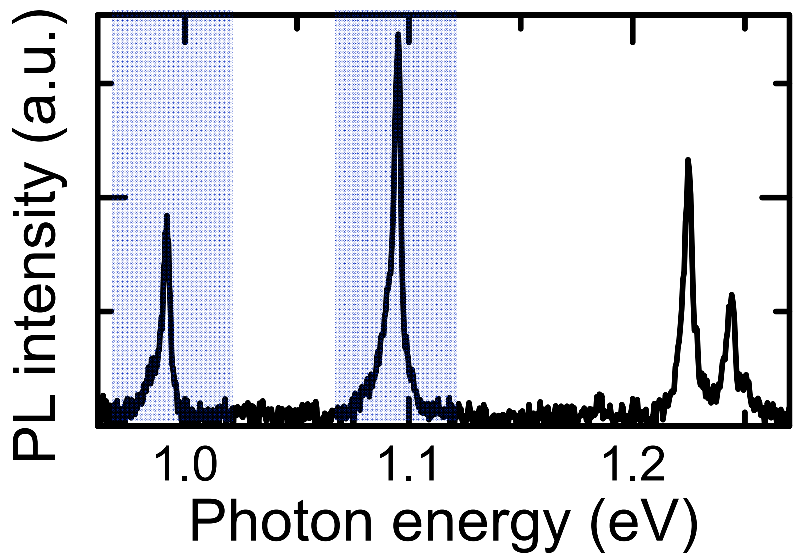
exciton: 1D



Current Project

Realization of Telecom Range (1300 - 1550 nm) Single Photon Source from SWCNTs at Room Temperature

- Air stable oxygen-doped SWCNTs
- Photon statistics of 1100 nm and 1300 nm peaks



Acknowledgements:

Han Htoon
Stephen Doorn
Sergei Tretiak
Andrei Piryatinski
Jinkyoung Yoo
Jared Crochet
Benjamin Mangum
Juan Duque
Xiaoying Pang
Feng Wang
Oleksiy Roslyak
Hisato Yamaguchi
Lyudmyla Adamska

Thanks for your attention!